

EFFECT OF PRESSURE ON AZEOTROPIC TEMPERATURE AND COMPOSITION

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CHANDRA PRAKASH AGARWAL

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CERTIFICATE

It is certified that this work has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

Date: 9th July 1973

Mamata Mukhopadhyay
Dr. M. Mukhopadhyay
Assistant Professor
Department of Chemical Engg.
Indian Institute of Technology
Kanpur-208016, India

POST GRADUATE OFFICE
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NOMENCLATURE

A, B, C	Antoine Constants
A_1, B_1	Redlich-Kister constants
A_2, B_2	Van-Laar constants
A_3, B_3	Scatchard-Hammer constants
A_{12}	Constants in the case of regular solutions.
B_{11}, B_{22}	Virial coefficients of component one- and two respectively.
B_{12}	Interaction virial coefficient of the mixture
G^E	Excess Gibbs free energy
$\Delta H_1, \Delta H_2$	Partial molal vaporization enthalpies of component one and two respectively.
ΔH_V	Change in heat of vaporization of the azeotrope
n_1, n_2	Number of moles of component one and two respectively.
n_T	Total number of moles in the mixture
P	Total pressure
P_1^0, P_2^0	Vapor pressures of component one and two respectively.
P_Z	Total pressure at azeotropic temperature
R	Universal gas constant
$\Delta S_1, \Delta S_2$	Change in entropy of vaporization of component one and two respectively.
ΔS_0	Total change in entropy of vaporization
T	Temperature
T_1, T_2	Boiling points of component one and two respectively.
T_{az}	Azeotropic temperature

T_c	Critical temperature
T_r	Reduced temperature
VL_1, VL_2	Molar liquid volume of component one and two respectively
ΔV_v	Volume change in vaporization of the azeotrope
x_1, x_2	Mole fraction of component one and two respectively in liquid phase.
Y_1, Y_2	Mole fraction of component one and two respectively in vapor phase
b	Packing factor
γ_1, γ_2	Activity coefficients of component one and two respectively.

ABSTRACT

A method has been developed for prediction of azeotropic data at different pressures from knowledge of the azeotropic data at a particular pressure. The Gauss-Seidel iterative technique is used on computer for solving the mathematical equations developed. The non ideality in the vapor phase is incorporated in terms of the virial equation of state and the excess free energy of mixing is calculated using any one of the correlations such as: R-K equation, Van-Laar equation and Scatchard-Hammett equation. The method has been verified using data from the literature for the systems: Ethyl alcohol-Ethyl acetate, Benzene-Cyclohexane, Hexane-Benzene, Methyl alcohol-Benzene, Ethyl alcohol-Methylcyclohexane and Ethyl alcohol-water. The predicted azeotropic temperatures and compositions are found to be in very good agreement with the experimental values except for highly nonideal systems comprising polar components in which maximum absolute error is 4%.

CHAPTER 1

INTRODUCTION

An azeotrope is a constant boiling mixture in which the vapour and liquid phases in equilibrium have the same composition, because of which components can not be separated by simple distillation.

Formation of azeotropes is a common phenomenon in industrial separation processes which makes one interested in the study of their vapour-liquid equilibrium behaviour. It is often observed for certain systems to exhibit either vapour pressure extremum under isothermal conditions or boiling temperature extremum under isobaric conditions. The azeotropic composition corresponds to either of these extremum points.

Azeotropes may be classified broadly into Homo and Heteroazeotropes depending upon the number of liquid phases present in the azeotrope. In the case of Homoazeotropes, components of the mixture are completely miscible with each other resulting in a single liquid phase whereas in the case of Heteroazeotropes, components are partially miscible resulting in more than one liquid phase. The mixtures however may change from one form to the other on varying the temperature over a certain range. Azeotropes may be further classified into positive and negative types. A positive azeotrope has a minimum

boiling point at constant pressure or maximum vapour pressure at constant temperature. Conversely, a negative azeotrope has a maximum boiling point and a minimum vapour pressure as shown in Fig. (1-1). Saddle (positive-negative) azeotropes are those azeotropes in which both maximum and minimum boiling points appear for a particular system at different compositions. They usually appear in multicomponent systems.

The azeotrope formation generally occurs when boiling points of the components lie within a certain range. Azeotropes are formed because of high nonideality in mixtures. If components differ largely in their molecular structures, sizes and chemical nature, the chances of formation of azeotropes are quite significant. It is also observed that in the case of binary mixtures, if the boiling points of the two components are identical, the azeotropic composition is approximately 50 mole per cent and shifts to the right or left when the boiling point of the component 2 is below or above that of 1. Azeotrope formation over a pressure range will depend upon the temperature coefficients of the vapour pressures, i.e. dP/dt of the two components. If the coefficient for component 1 (more volatile) is much greater or less than that of 2, the azeotrope disappears before the critical region is reached as shown in Figure (1-2). The dotted lines show the locus of the azeotropes. If the coefficients of the components are about the same, the azeotrope is terminated in the critical region as shown in

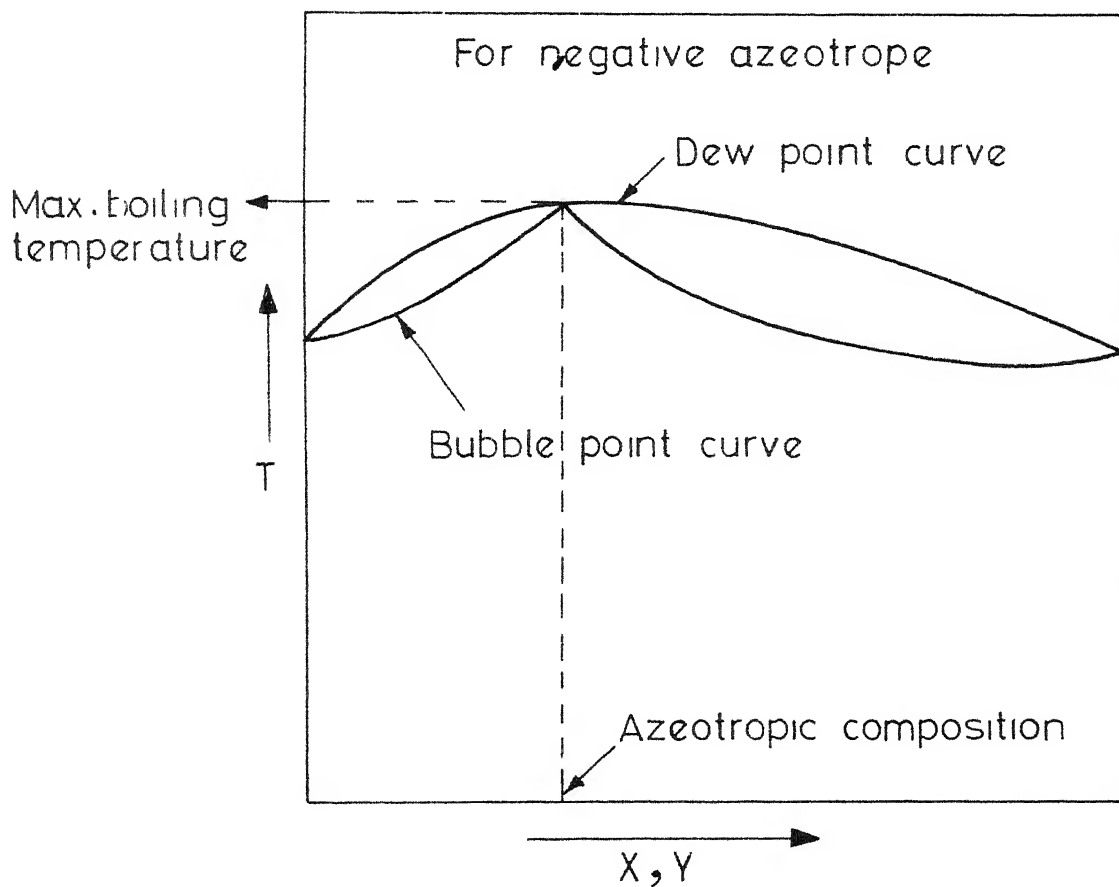
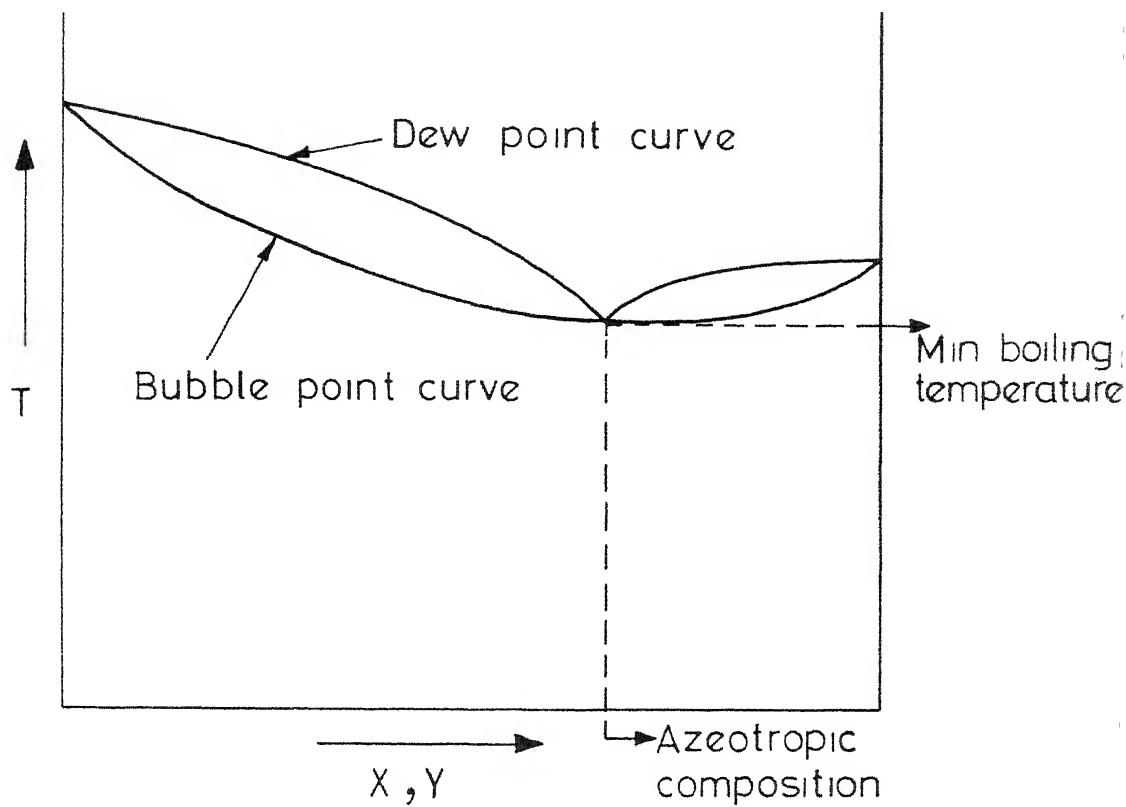
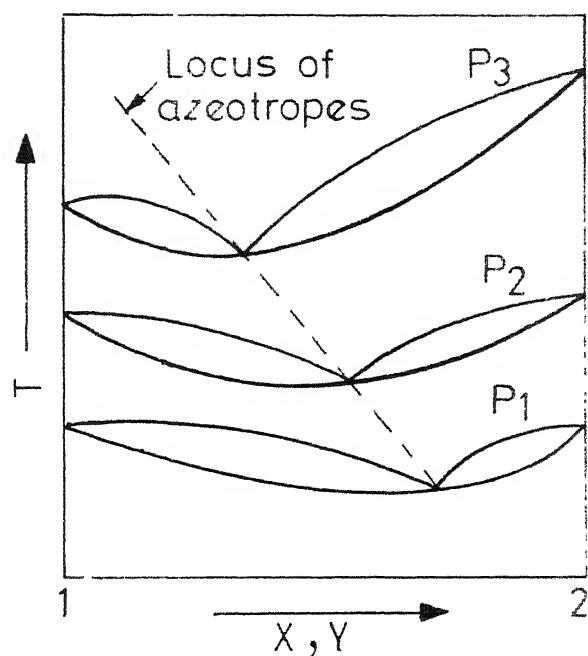
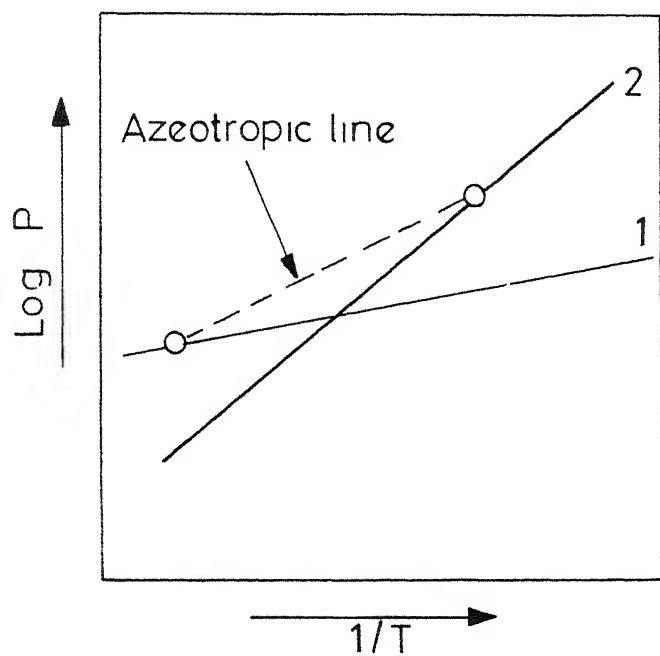


FIG 11 EQUILIBRIUM DIAGRAMS OF AZEOTROPES



For $\frac{\partial P_1}{\partial T} > \frac{\partial P_2}{\partial T}$

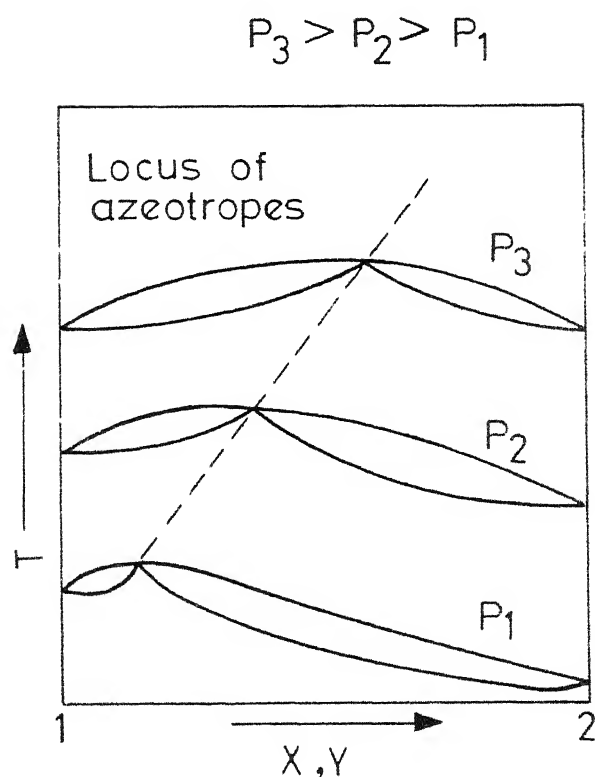
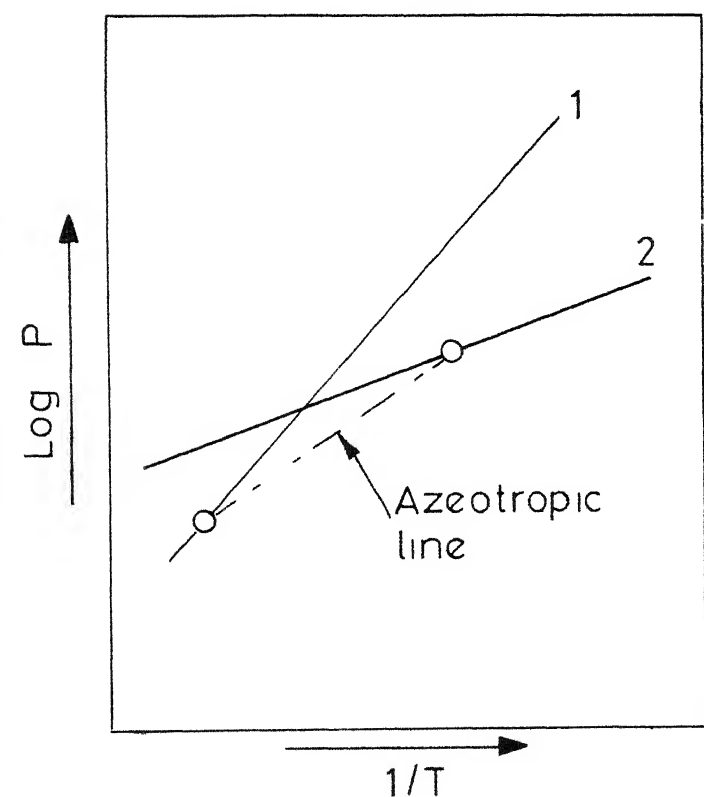


FIG.1.2 EFFECT OF PRESSURE ON AZEOTROPIC TEMPERATURE AND COMPOSITION.

Figure (1-3). This is called the critical azeotrope. In the critical region the critical locus curve (i.e. T_c vs x) is characterized by a minimum temperature point which not necessarily represents the critical azeotrope. A point of maximum and or minimum pressure in the critical locus curve (P_c vs x) may also exist when the composition of the critical azeotrope is rich in one of the components. Azeotropes formed in the critical region, only for those compounds whose critical temperatures do not differ by more than a characteristic value depending upon the chemical nature of the compounds under study.

The azeotropic behaviour of a system is studied by knowing its pressure-temperature and composition relationship or in other words the azeotropic P-T-x space. Once the azeotropic P-T-x space is known, one can separate the components either by varying the pressure or temperature, or by changing the composition. The composition can be changed by adding one of the components in excess or a third component to the mixture.

Most of the azeotropic pressure temperature composition data available in the literature are at atmospheric pressure. Very limited data are available at pressures other than atmospheric pressure. In the absence of a good method or a correlation for predicting the azeotropic P-T-x space over a wide range of pressures an attempt has been made in this

$$\text{FORT } \frac{\partial P_1}{\partial T} = \frac{\partial P_2}{\partial T}$$

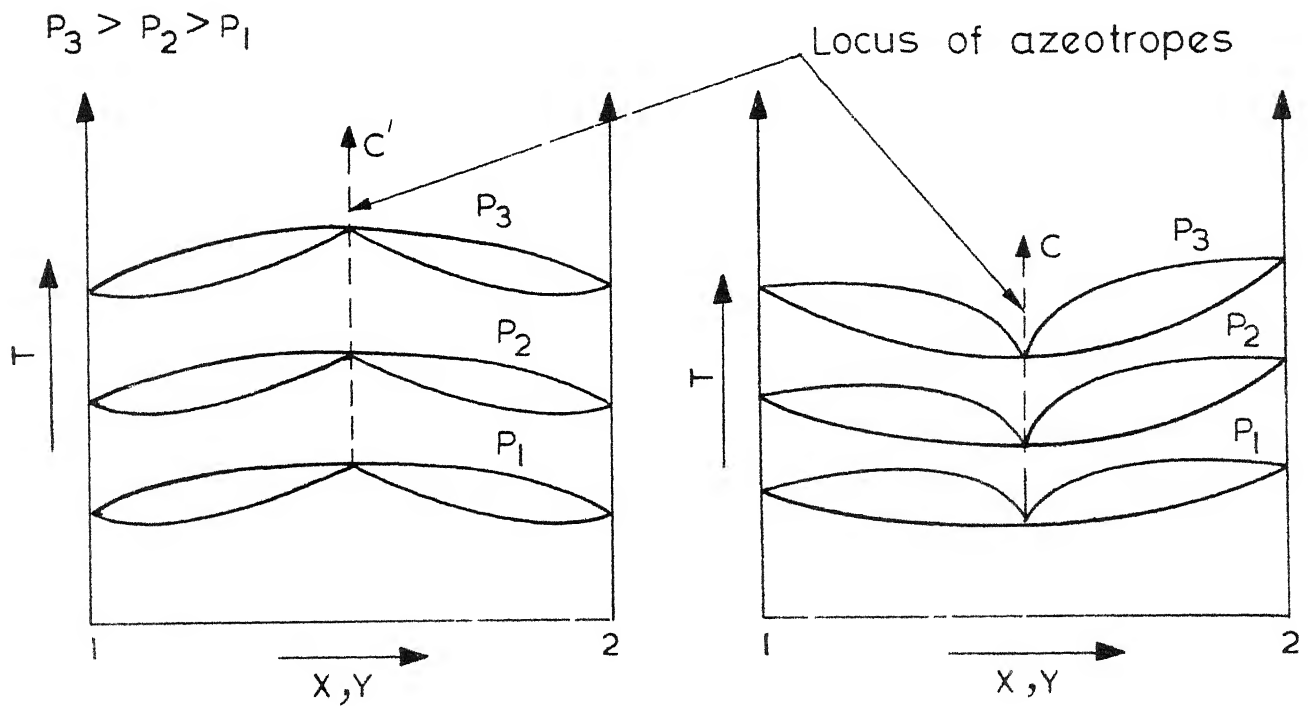
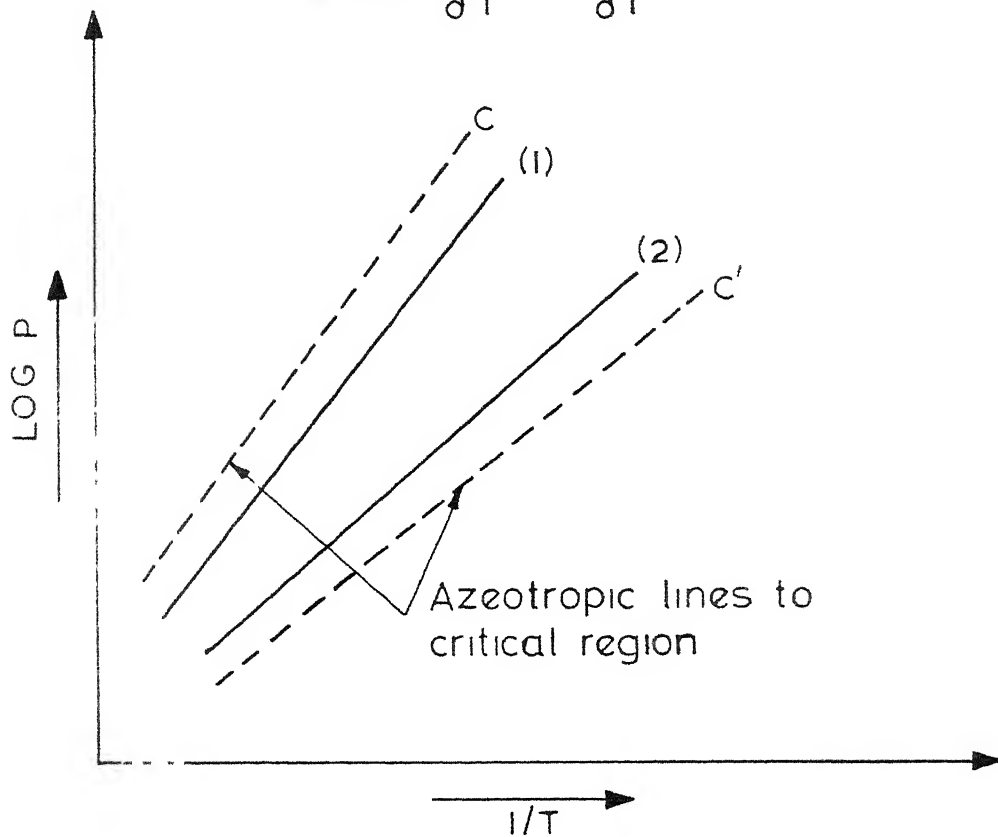


FIG 1 3 AZEOTROPES IN CRITICAL REGION

study to develop a theoretically sound method for accurate prediction of these data.

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CHAPTER 2

LITERATURE REVIEW

Dalton was the first person to observe the occurrence of a minimum vapour pressure while distilling aqueous solutions of hydrochloric acid and nitric acid. He observed that the boiling temperature and composition of distillates remained constant and also the boiling temperature was always higher than that of the higher boiling component. Roscoe attributed this phenomenon to the formation of a new chemical compound which caused the lowering of total vapour pressures. Between 1881 and 1884 the Russian chemist Konovalov observed the occurrence of minimum and maximum vapour pressures in the mixtures for which equilibrium liquid and vapour compositions were identical, and the maximum vapour pressure associated with the minimum boiling temperature and vice-versa. Later Storonkin observed this phenomenon in multicomponent mixtures. In 1911 Wade and Merriman introduced the term AZEOTROPE to designate all such mixtures irrespective of the number of components. Azeotrope is a Greek word which means 'difficult to separate'.

Since Azeotropism is one of the most common manifestation of nonideality in liquid solutions, the pioneer thermodynamicists like Duhem, Marquies, Lehfeld and others attempted to explain the occurrence of azeotropes theoretically.

In 1910 the Russian scientist VREVSKI formulated a general rule for the effect of pressure on azeotropic composition of a binary system. According to this rule, for a positive azeotrope the concentration of the component with higher evaporation enthalpy is increased with pressure, on the other hand, for negative azeotropes under isothermal conditions the change in pressure produces a decrease in the concentration of the component having higher evaporation enthalpy. This rule can be thermodynamically explained by equation (2.1) which has been derived with two assumptions, namely (i) Molar volume of the liquid is assumed to be negligible in comparison with the molar volume of the vapour, and (ii) Vapour phase is assumed to behave like an ideal gas.

$$\frac{dx_1}{d \ln P} = \frac{\frac{1}{\Delta \bar{H}_1} - \frac{1}{\Delta \bar{H}_2}}{\left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{P,T} \left(\frac{\Delta \bar{H}}{x_2 \Delta \bar{H}_1 \Delta \bar{H}_2} \right)} \quad (2.1)$$

where; $\Delta \bar{H} = x_1 \Delta \bar{H}_1 + x_2 \Delta \bar{H}_2$ and, $\Delta \bar{H}_1$ and $\Delta \bar{H}_2$ are the partial molar vapourization enthalpy of the components in the mixture. Whenever activity coefficient is greater than unity, the denominator of equation (2.1) is found to be negative and hence according to the equation (2.1) The mole fraction of component 1 in the azeotropes increases with pressure provided $\Delta \bar{H}_1$ is greater than $\Delta \bar{H}_2$.

Lecat (1918-1928) carried out numerous experiments on

azeotropes using highly pure chemicals and compiled extensive data known till then. Later in 1947 and 1948 Horsley compiled all experimental data known to date on binary and ternary zeotropes (non-azeotropes) as well as azeotropes.

In 1929 Lecat showed that the relation between the pressure and boiling temperatures of the azeotrope is similar to that for a pure compound. It may be represented to a close approximation by the equation (2.2),

$$\log P = A - B/T \quad (2.2)$$

where A and B are constants characteristic of the system.

Prigogine²¹ employed claussius-Clapeyron equation (2.3) to predict pressure-temperature relationship of azeotropes assuming heat of vaporization of the azeotrope to be independent of temperature i.e.

$$\frac{dT}{dP} = \frac{T \Delta V_v}{\Delta H_v} \quad (2.3)$$

where, ΔH_v = heat of vaporization of the azeotrope and ΔV_v = volume change in vaporization of the azeotrope.

Later Nutting and Horsley made use of the Cox-chart to predict azeotropic pressure-temperature relationship.

An approximate method for estimating the effect of temperature on azeotropic composition was suggested by Carlson and Colburn⁶. This method was based on the assumption that the ratio of the activity coefficients is independent of temperature and also that the vapour phase to behave like an ideal gas.

Hence the ratio of the activity coefficients is given by equation (2.4),

$$\frac{\gamma_1}{\gamma_2} = \frac{P_2^0}{P_1^0} \quad (2.4)$$

where, $\gamma_1, \gamma_2, P_1^0, P_2^0$ are the activity coefficients and vapour pressures of components 1 and 2. According to this method values of $\frac{\gamma_1}{\gamma_2}$ are plotted against the liquid composition, x_1 for a known temperature and on the same plot, values of P_2^0/P_1^0 are plotted against temperature using the same ordinate scale (Figure 2.1). From this plot azeotropic composition at any desired temperature can be obtained by making use of the azeotropic condition i.e. $\gamma_1/\gamma_2 = P_2^0/P_1^0$. The method is demonstrated by the dotted lines in Figure 2.1. For estimation of the total pressure corresponding to various azeotropic compositions and temperatures the following empirical expression was suggested:

$$P_Z = \frac{P'_Z (x_1 P_1 + x_2 P_2)}{(x_1^1 P_1^1 + x_2^1 P_2^1)} \quad (2.5)$$

where, P_Z, P'_Z = total vapour pressures of the azeotrope at the desired temperature, t and the reference temperature, t' .

P_1^1, P_2^1 = vapour pressures of the pure components 1 and 2 at the reference temperature, t' .

x_1, x_2 = mole fractions of components 1 and 2 in the azeotrope at t .

x_1^1, x_2^1 = mole fractions of components 1 and 2 at t' .

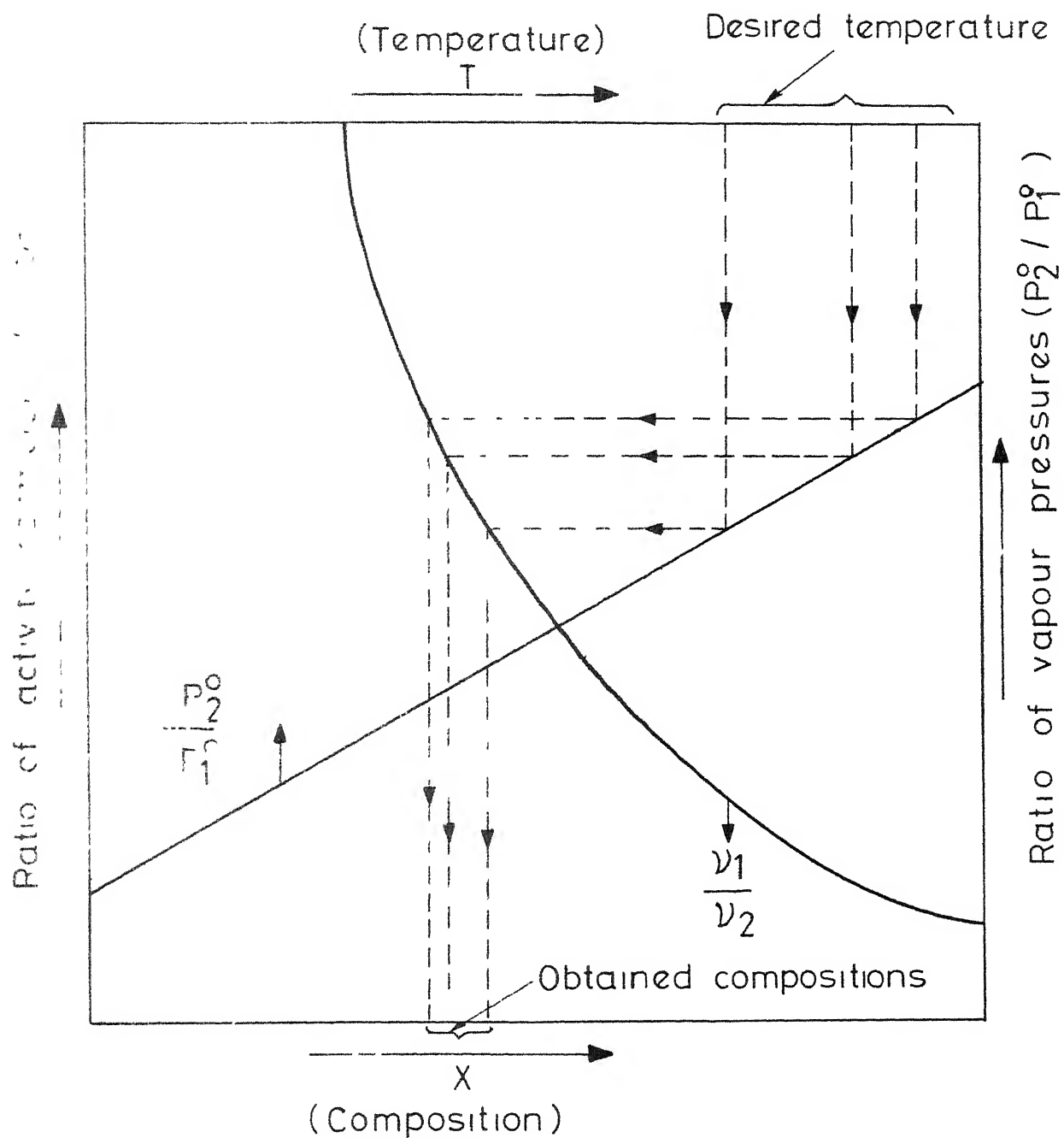


FIG.2.1 COULSON COLBURN METHOD FOR PREDICTION OF AZEOTROPIC COMPOSITION.

However the equation (2.5) finds little use as it often renders high inaccuracy in estimation of the total pressure.

Skolnic⁷ (1951) developed a graphical method for predicting pressure-temperature relationship of the azeotropes using the nomographs of Lippincott and Lyman⁸. These nomographs give vapour pressure-temperature relationship for pure compounds having normal boiling points between -50 and 550°C. Prior to it a modified form of the integrated Claussius-Clapeyron equation (2.6) was developed to depict the vapour pressure-temperature relationship.

$$\Delta t = \frac{(273.1 + t) (2.8808 - \log p)}{\emptyset + 0.15 (2.8808 - \log p)} \quad (2.6)$$

where, Δt = temperature in °C to be added to the observed temperature.

t = observed temperature

$(2.8808 - \log p)$ = Log of observed pressure subtracted from Log of standard pressure (760 mm of Hg.)

\emptyset = quantity proportional to entropy of vaporization at 760 mm of Hg.

The solution of equation (2.6) is found to be tedious and time consuming. To overcome this, Lippincott classified all the compounds into several groups according to their resemblance in physical and structural properties and presented nomographs to get vapour pressure-temperature relationship

knowing only the normal boiling temperature of the compound under consideration. It was observed that the average absolute deviation of the boiling temperature of pure compounds obtained from the nomographs from the experimental values is 0.9°C .

Use of Lippincott's nomographs was extended to the production of azeotropic pressure-temperature relationship. Because an azeotrope is a mixture of either two or more components, usually of widely different physical and structural properties, it is classified under component groups. Let us illustrate the method for an azeotrope whose components belong to groups 3 and 8. If the normal boiling point of the azeotrope is denoted by $\theta^{\circ}\text{C}$ and the reference pressure by P_0 , Then the pseudo boiling points of the components at this pressure are given by t_1 and t_2 as shown in Figure 2.2. Then corresponding to these temperatures points C and A are plotted in Figure 2.3 and D corresponds to normal azeotropic point. Finally distance CA is divided at point B in the ratio of the compositions of the two components known at standard pressure. Hence path DB represents pressure-temperature relationship for the azeotropic system.

This is obviously an approximate method as it is known that composition changes significantly with pressure. However, it was observed that for most of the azeotropic systems, this approximation does not lead to significant error in estimation. The deviation of the predicted temperature from the experimen

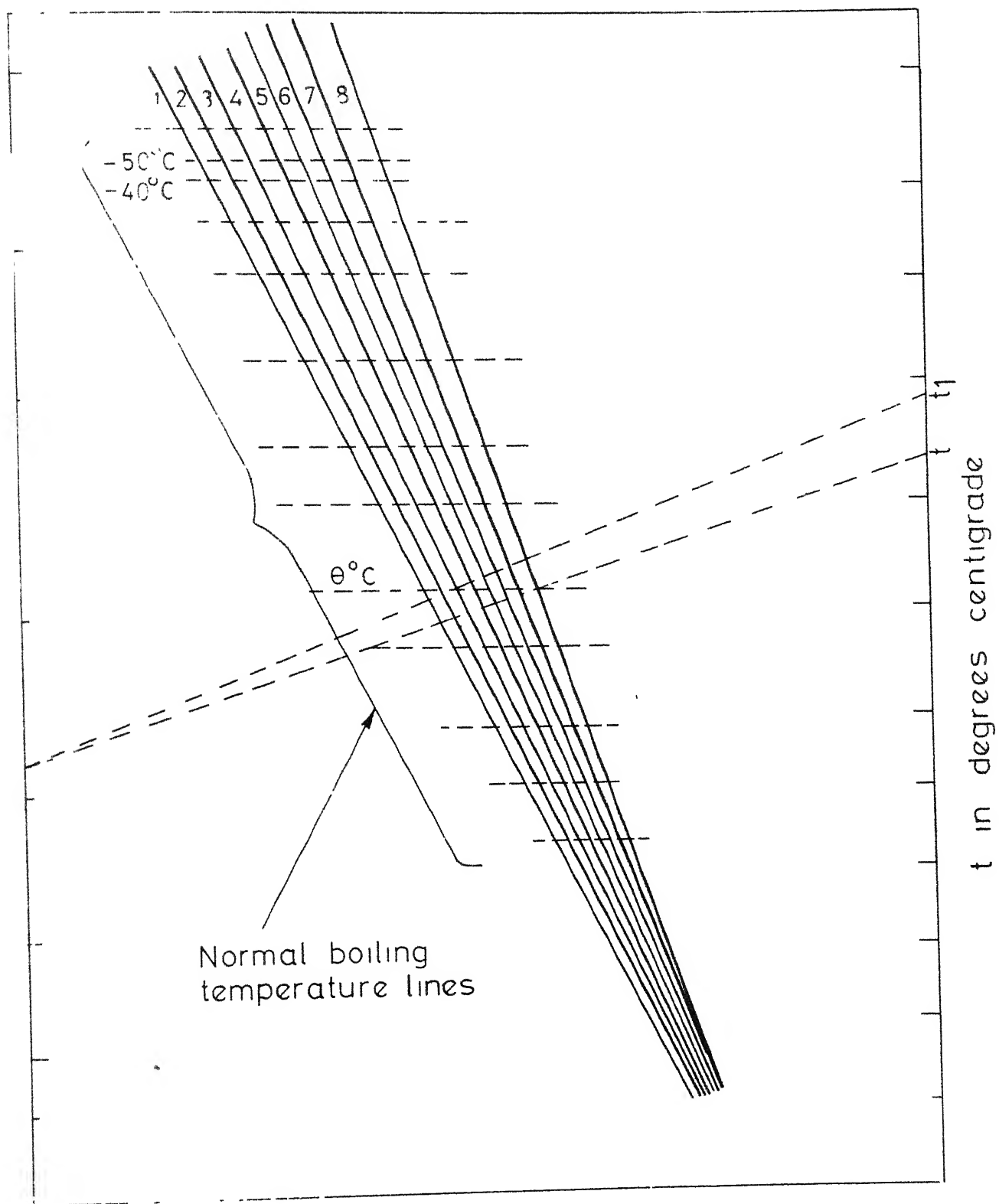


FIG. 2.2 LIPPINCOTT-LYMAN NOMOGRAPH

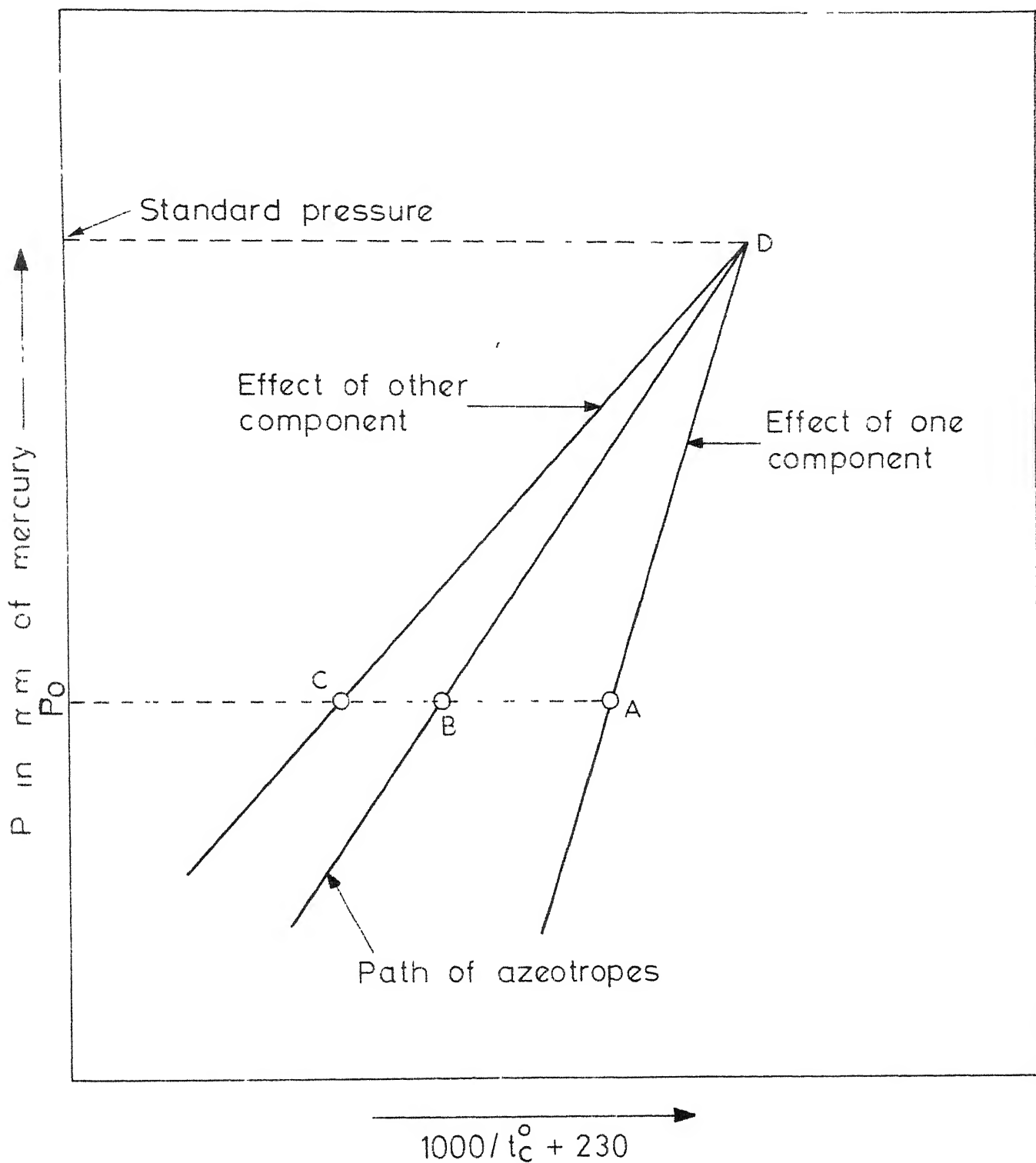


Fig 2.3 SKOLNIC'S APPROXIMATE METHOD FOR AZEOTROPIC PRESSURE TEMPERATURE RELATIONSHIP.

value is of the order of 1°C. The method is useful only at subatmospheric pressures and has limitations namely, the normal boiling temperature of the azeotrope must be known and if the components of the azeotrope belongs to same group then this method can not be used for prediction of the P-T-x data. The method obviously fails for systems for which azeotropes form only at pressures above atmospheric. Once the pressure-temperature relationship is known, the azeotropic composition is obtained from the linear relationship assumed by Skolnic for low pressures:

$$\log x = A - BT \quad (2.7)$$

where, x = mole percent of one component in the azeotrope

T = boiling temperature in °C of the azeotrope

A,B = constants for a particular system.

This technique was also tried for some multicomponent system but yielded poor agreement compared to binary systems.

Bandarajan⁹ of IIT/Madras also suggested a method for prediction of pressure-temperature relationship in Binary systems comprising non-polar as well as polar compounds from the pure component properties, such as molal latent heats of vaporization, molar volumes, vapour pressures etc. Reed's method was used for prediction of the azeotropic behaviour of non-polar mixtures. However, when the method was used for polar mixtures, the deviation of the predicted values from the experimental ones were quite large. Hence a method was developed

to relate these deviations to the dipole moments of the components. The agreement in boiling temperatures was found to range from within ± 0.3 to 3°C .

Thus an extensive literature survey on the existing methods for prediction of azeotropic pressure-temperature-composition data reveals that the methods are either empirical in nature or very complicated and time consuming. Most of the methods have been used at the low pressure range and yield inaccurate results. Hence it is decided to develop a method, for predicting the azeotropic P-T-x from the knowledge of one azeotropic point, which is theoretically sound having least assumptions and yet would yield better agreement compared to the existing methods.

CHAPTER 3

THEORETICAL CONSIDERATIONS

According to the phase rule there is only one degree of freedom for a binary azeotrope. Hence the P-T-x data for an azeotropic system is unique if any one of these three variables is specified. In order to know the effect of one of these variables over the others for the azeotropes, the present analysis is divided into two broad classes:

- (i) Prediction of T knowing P and x.
- (ii) Prediction of T and x at different values of P.

The prediction of the P-T-x space for both the classes is based on Redlich-Kister (3.1), Van-Laar (3.2) and Scatchard-Hammer (3.3) equations of third order for excess Gibbs free energy. The equations are as follows:

$$G^E = RTx_1x_2 \left[A_1 + B_1 (x_1 - x_2) \right] \quad (3.1)$$

$$G^E = RT \left\{ \frac{A_2 x_1 x_2^2}{\left(\frac{A_2}{B_2} x_1 + x_2 \right)^2} + \frac{B_2 x_2 x_1^2}{\left(x_1 + \frac{B_2}{A_2} x_2 \right)^2} \right\} \quad (3.2)$$

$$G^E = RT \left[x_1 \left\{ Z_2^2 (A_3 + 2Z_1 (B_3 \frac{V_{L1}}{V_{L2}} - A_3)) \right\} + x_2 \left\{ Z_1^2 (B_3 + 2Z_2 (A_3 \frac{V_{L2}}{V_{L1}} - B_3)) \right\} \right] \quad (3.3)$$

$$\text{where, } Z_1 = \frac{x_1}{x_1 + x_2} \frac{VL_2}{VL_1}, \quad Z_2 = \frac{x_2}{x_1 + x_2} \frac{VL_2/VL_1}{VL_1}$$

For the regular solutions these equations reduce to the following form:

$$G^E = A_{12} x_1 x_2 \quad (3.4)$$

Here the constant A_{12} is independent of temperature. In the present study the temperature dependence of the constants in the equations (3.1) to (3.3) is assumed to be as follows:

$$T_1(A_i)_{T_1} = T_2(A_i)_{T_2} \quad (3.5)$$

$$T_1(B_i)_{T_1} = T_2(B_i)_{T_2} \quad (3.6)$$

where, $i = 1, \dots, 3$.

This temperature dependence of the constants is based on the regular solution theory which essentially presumes the product $T \ln \gamma_i$ constant. From these expressions of G^E one can obtain the activity coefficients using the following relation:

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P,n_j} = \frac{1}{RT} \left(\frac{\partial (n_T G^E)}{\partial n_i} \right)_{T,P,n_j}; \quad n_T = n_1 + n_2 \quad (3.7)$$

which can be used in predicting the P-T-x space of the azeotropes. The expressions thus obtained for activity coefficients are as given below:

For R-K Equation:

$$\ln \gamma_1 = x_1 x_2 \left[A_1 + B_1 (x_1 - x_2) \right] + x_2 \left[A_1 (x_2 - x_1) + B_1 (6x_1 x_2 - 1) \right] \quad (3.8)$$

$$\ln \gamma_2 = x_1 x_2 \left[A_1 + B_1 (x_1 - x_2) \right] - x_1 \left[A_1 (x_2 - x_1) + B_1 (6x_1 x_2 - 1) \right] \quad (3.9)$$

For Van-Laar Equation:

$$\ln \gamma_1 = \frac{A_2 x_2^2}{\left(\frac{A_2}{B_2} x_1 + x_2 \right)^2} \quad (3.10)$$

$$\ln \gamma_2 = \frac{B_2 x_1^2}{\left(x_1 + \frac{B_2}{A_2} x_2 \right)^2} \quad (3.11)$$

For Scatchard-Hammet Equation:

$$\ln \gamma_1 = Z_2^2 \left[A_3 + 2Z_1 \left(B_3 \frac{V_{L1}}{V_{L2}} - A_3 \right) \right] \quad (3.12)$$

$$\ln \gamma_2 = Z_1^2 \left[B_3 + 2Z_2 \left(A_3 \frac{V_{L2}}{V_{L1}} - B_3 \right) \right] \quad (3.13)$$

For estimation of activity coefficients, it is needed to evaluate the constants of these equations by rearranging the respective equations. It requires the values of the activity coefficients at some known pressure-temperature and composition. For this the activity coefficients are calculated assuming the vapour phase in equilibrium with the liquid phase to be a nonideal mixture. The equations are:

$$\ln \gamma_1 = \ln \left(\frac{P_{x_1}}{P_{1x_1}^0} \right) + \frac{1}{RT} \left[(B_{11} - V_{L1})(P - P_1^0) + P \left(\frac{1}{2} Y_2^2 \right) \right] \quad (3.14)$$

$$\ln y_2 = \ln (P^{y_2}/P_2^0 x_2) + \frac{1}{RT} \left[(B_{22} - V L_2)(P - P_2^0) + P \zeta_{12} y_1^2 \right] \quad (3.15)$$

$$\text{where } \zeta_{12} = 2B_{12} - B_{11} - B_{22}$$

Here the interaction virial coefficient B_{12} is assumed to be the harmonic mean of the individual virial coefficients, B_{11} and B_{22} , i.e.:

$$\frac{2}{B_{12}} = \frac{1}{B_{11}} + \frac{1}{B_{22}} \quad (3.16)$$

The equations (3.14) and (3.15) require (i) P-T-x data instead of P-T-x-y data because $x = Y$, (ii) pure component vapour pressures P_1^0 , P_2^0 which are estimated by the Antoine equations, (iii) the second virial coefficients B_{11} and B_{22} which are predicted by employing the Kreglewski's ¹¹ double square well potential, and (iv) the pure liquid molar volumes VL_1 and VL_2 calculated by dividing the molecular weights by respective specific gravities because of the assumption that VL_1 and VL_2 do not change with temperature and pressure significantly and also VL_1 and VL_2 in comparison with B_{11} and B_{22} are quite small. Details of the equations used for the vapour pressure and the second virial coefficients evaluation are as follows:

(1) Antoine equation for vapour pressure calculation:

$$\log_{10} P = A - B/t + c \quad (3.17)$$

Constants A, B and c are obtained from the literature for a

particular pure component under consideration.

(11) Kreglewskis¹¹ model gives the following equations for estimation of the second virial coefficients, B_{11} and B_{22} :

$$\frac{B_{11}}{bV^*} = 1 - (R_1 - 1)(e^{-u/kT} - 1) - (R_2 - R_1)(e^{-su/kT} - 1) \quad (3.18)$$

where, R_1 and R_2 are given by the following expressions:

$$R_1 = \left[1 + \frac{s}{(V^*)^{1/3}} \right] \quad (3.19)$$

$$R_2 = \left[1 + \left(\frac{V_0^*}{V^*} \right)^{1/3} \right]^3 \quad (3.20)$$

Here, V_0^* is the liquid molar volume of methane at reduced temperature, $T_r = 0.6$; s is a constant and is equal to 0.21 rounded off for all the substances and V^* is the liquid molar volume of the compound under consideration at $T_r = 0.6$. The potential energy term u/kT is estimated by:

$$-u/kT = \frac{\rho}{RT} E^* \times 0.239 \quad (3.21)$$

where, ρ is the density and is assumed to be constant at 0.32, E^* is the energy term and can be obtained from the literature¹¹ for a particular compound, 0.239 is a conversion factor used and T is the temperature at which the virial coefficients are to be calculated. The packing factor, b is estimated by the equation (3.22), i.e.:

$$b = 0.77 + 0.1325 (T_c)^{1/3} \quad (3.22)$$

where, T_c is the critical temperature of the pure compound under consideration.

From the knowledge of the activity coefficients at one point, the constants in the equations (3.1) to (3.3) can be obtained by the following expressions:

$$A_1 = \frac{\ln \gamma_1}{x_2^2} - \frac{(x_1^2 x_2 + 5x_1 x_2^2 - x_2) B_1}{x_2^2} \quad (3.23)$$

$$B_1 = \left(\frac{\ln \gamma_1}{x_2^2} - \frac{\ln \gamma_2}{x_1^2} \right) / \left(\frac{x_1^2 x_2 + 5x_1 x_2^2 - x_2}{x_2^2} - \frac{x_1 - x_1 x_2^2 - 5x_1^2 x_2}{x_1^2} \right) \quad (3.24)$$

$$A_2 = \log \gamma_1 \left(1 + \frac{x_2 \log \gamma_2}{x_1 \log \gamma_1} \right)^2 \quad (3.25)$$

$$B_2 = \log \gamma_2 \left(1 + \frac{x_1 \log \gamma_1}{x_2 \log \gamma_2} \right)^2 \quad (3.26)$$

$$A_3 = \frac{\ln \gamma_2}{2Z_1^2 Z_2 \frac{V_{L2}}{V_{L1}}} - \frac{B_3 (1 - 2Z_2)}{2Z_2 \frac{V_{L2}}{V_{L1}}} \quad (3.27)$$

$$B_3 = \frac{\frac{\ln \gamma_1}{Z_2^2 (1 - 2Z_1)} - \frac{\ln \gamma_2}{2Z_1^2 Z_2 \frac{V_{L2}}{V_{L1}}}}{\left(\frac{2Z_1 \frac{V_{L1}}{V_{L2}}}{(1 - 2Z_1)} \right) - \left(\frac{1 - 2Z_2}{2Z_2 \frac{V_{L2}}{V_{L1}}} \right)} \quad (3.28)$$

Now for predicting the P-T-x space, G^E values are calculated using equations (3.1), (3.2) and (3.3). The azeotropic temperature can be obtained from the expression:

$$G^E = RT (x_1 \ln y_1 + x_2 \ln y_2) \quad (3.29)$$

Rearranging equations (3.14) and (3.15) one gets:

$$PY_1 = P_1^0 x_1 y_1 \exp \left\{ \frac{(VL_1 - B_{11})(P - P_1^0) - \epsilon_{12} y_2^2 P}{RT} \right\} \quad (3.30)$$

and $PY_2 = P_2^0 x_2 y_2 \exp \left\{ \frac{(VL_2 - B_{22})(P - P_2^0) - \epsilon_{12} y_1^2 P}{RT} \right\} \quad (3.31)$

Using equations (3.30) and (3.31) in (3.29) we have:

$$G^E = RT \left(x_1 \ln \frac{PY_1}{P_1^0 x_1 \exp U_1} + x_2 \ln \frac{PY_2}{P_2^0 x_2 \exp U_2} \right) \quad (3.32)$$

where, $U_1 = \frac{(VL_1 - B_{11})(P - P_1^0) - \epsilon_{12} y_2^2 P}{RT}$

and $U_2 = \frac{(VL_2 - B_{22})(P - P_2^0) - \epsilon_{12} y_1^2 P}{RT}$

equation (3.32) may be further simplified to:

$$G^E = RT \left(x_1 \ln \frac{P}{P_1^0} + x_2 \ln \frac{P}{P_2^0} + x_1 \ln \frac{y_1}{x_1} + x_2 \ln \frac{y_2}{x_2} - x_1 U_1 - x_2 U_2 \right) \quad (3.33)$$

or $G^E = RT (V + W - U) \quad (3.34)$

where, $V = x_1 \ln \frac{P}{P_1^0} + x_2 \ln \frac{P}{P_2^0}$

$$W = x_1 \ln \frac{y_1}{x_1} + x_2 \ln \frac{y_2}{x_2}$$

$$U = x_1 U_1 + x_2 U_2$$

Hence from equation (3.34) the azeotropic temperature is obtained from the simplified expression:

$$T = \frac{G^E}{(V+W-U)} \quad (3.35)$$

Equation (3.35) is implicit in T . Hence T can be obtained by an iterative procedure with the first approximation on the right hand side taken as $T = T_1x_1 + T_2x_2$. Further, computer calculations show that V is very sensitive to temperature and even a little off approximation for T on the right hand side makes the expression $(V+W-U)$ negative, yielding negative values of temperatures. To obviate this difficulty, v is expressed in a different form. The Clausius-Clapeyron equation can be expressed in terms of the entropy of vaporization as follows:

$$RT \ln P/P_1^0 = \Delta S_1(T_1 - T) \quad (3.36)$$

In this expression it is assumed that the molar heat of vaporization is constant over the temperature range under consideration. Here T_1 is the pure component boiling point at pressure P and ΔS_1 is the entropy of vaporization. Substituting this in equation (3.34), the following expression results:

$$G^E = x_1 \Delta S_1(T_1 - T) + x_2 \Delta S_2(T_2 - T) + RTW - RTU \quad (3.37)$$

Hence T can be obtained from equation (3.37), whose explicit form is as follows:

$$T = T_1x_1 \frac{\Delta S_1}{\Delta S_0} + T_2x_2 \frac{\Delta S_2}{\Delta S_0} - \frac{G^E}{\Delta S_0} + \frac{RTW}{\Delta S_0} - \frac{RTU}{\Delta S_0} \quad (3.38)$$

where, $\Delta S_0 = x_1 \Delta S_1 + x_2 \Delta S_2$

This is the final expression which will be used for the prediction of T in the azeotropic P - T - x space.

For prediction of T knowing P and x , as a first approximation, T is obtained as $(T_1x_1 + T_2x_2)$. The entropies are calculated from equation (3.36). The value of G^E will be calculated from equations (3.1) to (3.3) separately. Here U is the expression for nonideality in the vapor phase. The term involving W in equation (3.38) is neglected because of the reason that for an azeotrope $x = Y$. Also in equations (3.14) and (3.15) Y_1 and Y_2 are replaced by x_1 and x_2 respectively.

For the prediction of T and x at different values of P , all the above equations are used. The procedure for this type of prediction is as follows:

Suppose P' is the pressure at which azeotropic composition and boiling temperature are desired. First of all corresponding to pressure, P' approximate azeotropic boiling temperature is obtained by the method given by Skolnic⁷ (Chapter 2). In case the components belong to the same group, then for estimation of T_1 and T_2 from nomographs, normal boiling temperatures of the pure compounds are used instead of the normal azeotropic boiling point. Now using this approximate azeotropic temperature, the values of the activity coefficients are obtained using equations (3.14) and (3.15) in which the last term containing composition of the vapor phase, Y is neglected, because of the fact that the term, $P \sum_{12} Y^2$ is very

small compared to the other terms. Further, equations (3.8) to (3.13) are used to calculate the activity coefficients at a number of assumed compositions, x and then they are matched with the activity coefficients obtained at the approximate boiling temperature, T using equations (3.14)-(3.15) as mentioned earlier. Hence corresponding to pressure, P' approximate values of temperature, T and composition, x are obtained. Finally these initial values of T and x are further improved using the iterative procedure described earlier, checking in between whether x approximately equals Y and also whether the term W in equation (3.38) goes to a very small value.

For these two type of predictions as stated above computer programs have been developed to determine the P - T - x space of the azeotropes.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter the results of two ways of predicting azeotropic data namely (i) azeotropic temperature knowing azeotropic pressure-composition and (ii) azeotropic temperature and composition at different pressures will be presented. For both types of prediction azeotropic (P-T-x) data are necessary at one point. Analysis of the methods and all necessary equations are presented in Chapter 3. The first kind of prediction is essentially to test the prediction methods for their accuracy as it is known that both temperature and composition are unique at a fixed pressure. The equations used for the two kinds of predictions are essentially the same. The Gauss-Siedel iterative technique is employed for solving these equations on computer and is briefly described in Appendix A. The computer program for the two types of predictions are given in Appendix B.

In order to test the validity of the prediction methods, the systems chosen are diversified in their physical and structural properties. They belong to the groups: aromatics-paraffins, aromatics naphthenes, hydrocarbon-alcohol, e s t e r - alcohol and alcohol-water. For all these systems azeotropic data were available in the literature. The physical properties¹² needed for calculation of the activity coefficients are presented in Table 1. These properties have been predicted using the methods mentioned in Chapter 3, wherever experimental

TABLE 1

PHYSICAL PROPERTIES OF PURE SUBSTANCES

Sl. No.	Compound	Mole wt.	NBP °K	Antoine Constants	T _c , °K	Sp. gr.	V _L , cc/mole
1.	Benzene (C ₆ H ₆)	78.0	353.2°	A=6.90565 B=1211.033 C=220.790	562.0°	0.5790	88.7372
2.	Ethyl acetate (C ₄ H ₈ O ₂)	88.0	350.1	A=7.10232 B=1245.239 C=217.911	523.3°	0.9010	97.6804
3.	Methyl-cyclohexane (C ₇ H ₁₄)	98.0	373.9°	A=6.82689 B=1272.864 C=221.630	572.1	0.7690	127.4382
4.	Hexane (C ₆ H ₁₄)	86.0	341.8°	A=6.87776 B=1171.330 C=224.366	507.3°	0.65937	130.4275
5.	Cyclohexane (C ₆ H ₁₂)	84.0	353.8°	A=6.88817 B=1229.973 C=224.103	553.4	0.7790	107.8306
6.	Ethylalcohol (C ₂ H ₆ O)	46.0	351.4°	A=8.16290 B=1623.220 C=228.980	516.2	0.7890	58.3904
7.	Methylalcohol (CH ₄ O)	32.0	337.6°	A=8.07246 B=1574.990 C=238.860	512.5	0.7924	40.3836
8.	Water (H ₂ O)	18.0	373.1	A=7.96681 B=1668.210 C=228.000	647.3	1.0000	18.0000

data were not available. The constants in the equations of Redlich-Kister, Van-Laar and Scatchard-Hammer, have been obtained from knowledge of the activity coefficients at known compositions and they are presented in Table 2. The extent of nonideality and assymetry of the systems are manifested by the magnitude of these values.

The azeotropic temperatures predicted using the first type of prediction are presented in Table 3. Comparing these temperatures with the experimental values it is seen that the agreement is very good for nonpolar-nonpolar as well as polar-nonpolar systems. Relatively large deviations observed in the systems, comprising polar compounds may be attributed to the high nonideality caused by the association between the two components and strong dipole-dipole interactions. The values of activity coefficients, vapor pressures, virial coefficients, and constants of the three equations used at these predicted azeotropic temperatures are presented in Appendix - A.

The azeotropic temperatures and compositions obtained using the second type of prediction are presented in Tables 4 to 6. For this prediction approximate values of azeotropic temperatures, Figures (4.7) to (4.12) and ranges of compositions are first obtained by the method described in Chapter 3 and are presented in Tables 7 and 8 respectively. The computer program needed for approximating the azeotropic temperatures is given in Appendix B. From the comparison of the predicted

TABLE 2

VALUES OF THE CONSTANTS IN R-K, V-L, S-H EQUATIONS AT AZEOTROPIC TEMPERATURE

Sl. No.	System	P mm Hg	T _{az} °K	x _{1az}	γ_1	γ_2	R - K Constants	Van-Laar Constants	Scatchard-Hammer Constants
1.	Ethyl alcohol + ethylacetate	760.0	344.9	0.4610	1.2778	1.1810	A ₁ =0.8181 B ₁ =0.0306	A ₂ =0.7985 B ₂ =0.8501	A ₃ = 0.7690 B ₃ = 0.7696
2.	Benzene + Cyclohexane	759.0	350.5	0.5020	1.0817	1.1699	A ₁ =0.4709 B ₁ =-0.1530	A ₂ =0.6983 B ₂ =0.3552	A ₃ = 0.5940 B ₃ = 0.2781
3.	Hexane + Benzene	760.0	341.9	0.9630	0.9971	1.4176	A ₁ =1.2882 B ₁ =-1.0852	A ₂ =-0.0434 B ₂ = 0.2203	A ₃ = 4.8781 B ₃ = 0.2013
4.	Methyl alcohol + Benzene	676.4	328.1	0.6080	1.2979	2.0276	A ₁ =1.8511 B ₁ =-0.1076	A ₂ =1.9687 B ₂ =1.7472	A ₃ =1.6857 B ₃ =1.2431
5.	Ethyl alcohol + Methylcyclohexane	120.2	303.1	0.5400	1.5173	2.0319	A ₁ =2.2377 B ₁ =-0.2305	A ₂ =2.4996 B ₂ =2.0257	A ₃ =2.1539 B ₃ =1.0571
6.	Ethyl alcohol + Water	760.0	351.2	0.8940	1.0074	2.2880	A ₁ = 1.1453 B ₁ =-0.1904	A ₂ =1.5127 B ₂ =0.9564	A ₃ =0.0667 B ₃ =0.9552

TABLE 3

COMPARISON OF OBSERVED AND PREDICTED AZEOTROPIC TEMPERATURE

Sl. No.	System	P mm Hg.	x_{1az}	T _{az} ^{obs} °K	T _{az} ^{RKT} °K	T _{az} ^{VLT} °K	T _{az} ^{SHT} °K
1.	Ethyl alcohol ³ + ethyl acetate (polar - polar)	423.0 220.0 77.4	0.3980 0.3230 0.2660	329.4' 313.7' 291.9	329.9 314.6 293.1	329.9' 314.6' 293.1'	329.9 314.6 293.1
2.	Benzene ³¹ + cyclohexane (nonpolar - nonpolar)	600.0 206.0	0.4950 0.4940	343.1 313.2	343.2 313.7	343.2' 313.7	343.2 313.7
3.	Hexane ¹⁵ + Benzene (nonpolar - nonpolar)	735.0	0.9900	340.5'	340.8'	340.8'	340.8
4.	Methyl alcohol ²⁸ + Benzene (polar - nonpolar)	366.0	0.5500	313.2'	313.1	313.1	313.2
5.	Ethyl alcohol ¹⁵ + Methyl cyclohexane (polar - nonpolar)	41.3	0.4900	283.2	283.3	283.3	283.3
6.	Ethyl alcohol ^{29,30} + Water (polar - polar)	380.0 190.0 95.0 50.0	0.9480 0.8980 0.8900 0.8950	336.2' 323.0 309.2' 294.4	334.7 319.8 306.3 295.0	334.7 319.8 306.3 295.0	334.7 319.8 306.3 295.0

COMPARISON OF OBSERVED AND PREDICTED AZEOTROPIC TEMPERATURES AND COMPOSITIONS
USING R-K EQUATION

Sl. No.	System	P mm Hg.	Experimental Values		Predicted Values		
			T, °K	x _{1az}	T _{az} , °K	x _{1az}	x ₁ -y ₁
1.	Ethyl alcohol + Ethylacetate	423.0 220.0 77.4	329.5 313.7 291.9	0.3980 0.3230 0.2660	329.9 314.6 293.1	0.3970 0.3310 0.2355	0.0002 0.0000 0.0002
2.	Benzene + Cyclohexane	600.0 206.0	343.1 313.2	0.4950 0.4940	343.2 313.7	0.4985 0.4850	0.0002 0.0001
3.	Hexane + Benzene	735.0	340.5	0.9900	340.9	0.9595	0.0001
4.	Methyl alcohol + Benzene	366.0	313.2	0.5500	313.1	0.5805	0.0011
5.	Ethyl alcohol + Methyl cyclohexane	41.3	283.2	0.4900	283.3	0.4935	0.0000
6.	Ethyl alcohol + Water	380.0 190.0 95.0 50.0	336.2 323.0 309.2 294.4	0.9480 0.8980 0.8900 0.8850	334.7 319.8 306.3 295.0	0.8800 0.8735 0.8670 0.8610	0.0001 0.0001 0.0001 0.0002

TABLE 5

COMPARISON OF OBSERVED AND PREDICTED AZEOTROPIC TEMPERATURES AND COMPOSITIONS USING VAN-LAAR EQUATION

Sl. No.	System	P mm Hg	Experimental Values		Predicted Values		
			$T_{az}, ^\circ K$	x_{1az}	$T_{az}, ^\circ K$	x_{1az}	$ x_1 - y_1 $
1.	Ethyl alcohol + ethylacetate	423.0 220.0 77.4	329.5 313.7 291.9	0.3980 0.3230 0.2660	329.9 314.6 293.1	0.3970 0.3305 0.2355	0.0002 0.0002 0.0001
2.	Benzene + Cyclohexane	600.0 206.0	343.1 313.2	0.4950 0.4940	343.2 313.7	0.4980 0.4850	0.0002 0.0002
3.	Hexane + Benzene	735.0	340.5	0.9900	340.9	0.9610	0.0000
4.	Methyl alcohol + Benzene	366.0	313.2	0.5500	313.1	0.5800	0.0015
5.	Ethyl alcohol + Methylcyclohexane	41.3	283.2	0.4900	283.3	0.4930	0.0000
6.	Ethyl alcohol + Water	380.0 190.0 95.0 50.0	336.2 323.0 309.2 294.4	0.9480 0.8980 0.8900 0.8850	334.7 319.8 306.3 295.0	0.8795 0.8730 0.8660 0.8605	0.0001 0.0001 0.0001 0.0001

TABLE 6

COMPARISON OF OBSERVED AND PREDICTED AZEOTROPIC TEMPERATURES
AND COMPOSITION USING SCATCHARD-HAMMER EQUATION

Sl. No.	System	F mm Hg.	Observed Values		Predicted Values		
			$T_{az}, ^\circ K$	x_{1az}	$T_{az}, ^\circ K$	x_{1az}	$ x_1 - Y_1 $
1.	Ethyl alcohol + ethylacetate	423.0 220.0 77.4	329.5 313.7 291.9	0.3980 0.3239 0.2660	329.9 314.6 293.1	0.3990 0.3345 0.2390	0.0003 0.0001 0.0001
2.	Benzene + Cyclohexane	600.0 206.0	343.1 313.2	0.4950 0.4940	343.2 313.7	0.4990 0.4860	0.0001 0.0002
3.	Hexane + Benzene	735.0	340.5	0.9900	340.9	0.9600	0.0002
4.	Methyl alcohol + Benzene	366.0	313.2	0.5500	313.1	0.5850	0.0013
5.	Ethyl alcohol + Methylcyclohexane	41.3	283.2	0.4900	283.3	0.5010	0.0008
6.	Ethyl alcohol + Water	380.0 190.0 95.0 50.0	336.2 323.0 309.2 294.4	0.9480 0.8980 0.8900 0.8850	334.7 319.8 306.3 295.0	0.8795 0.8730 0.8665 0.8610	0.0002 0.0002 0.0002 0.0001

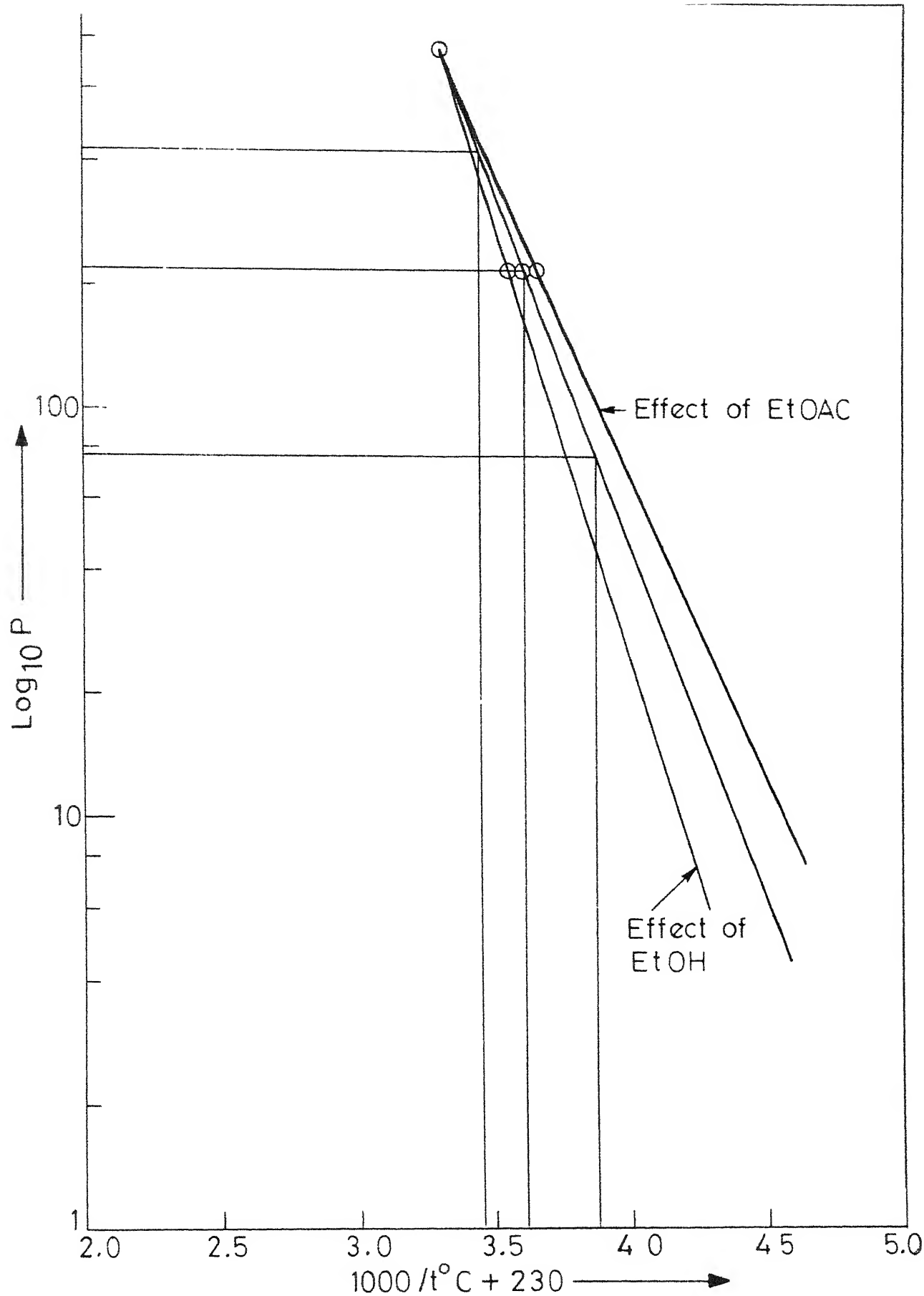


FIG.4 7 APPROXIMATION OF AZETROPIC TEMPERATURE FOR
SYSTEM ETHYL ALCOHOL-ETHYLACETATE

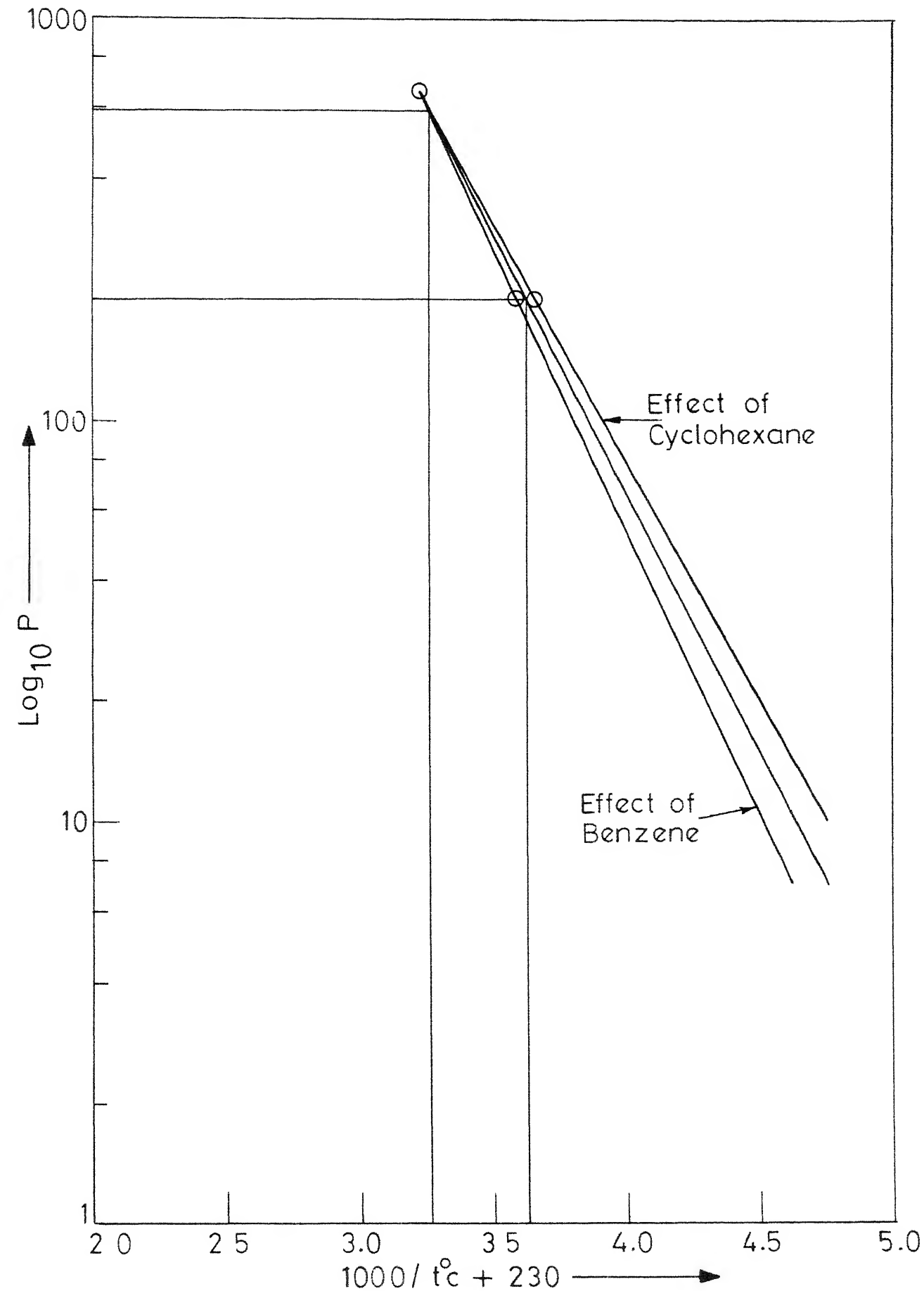
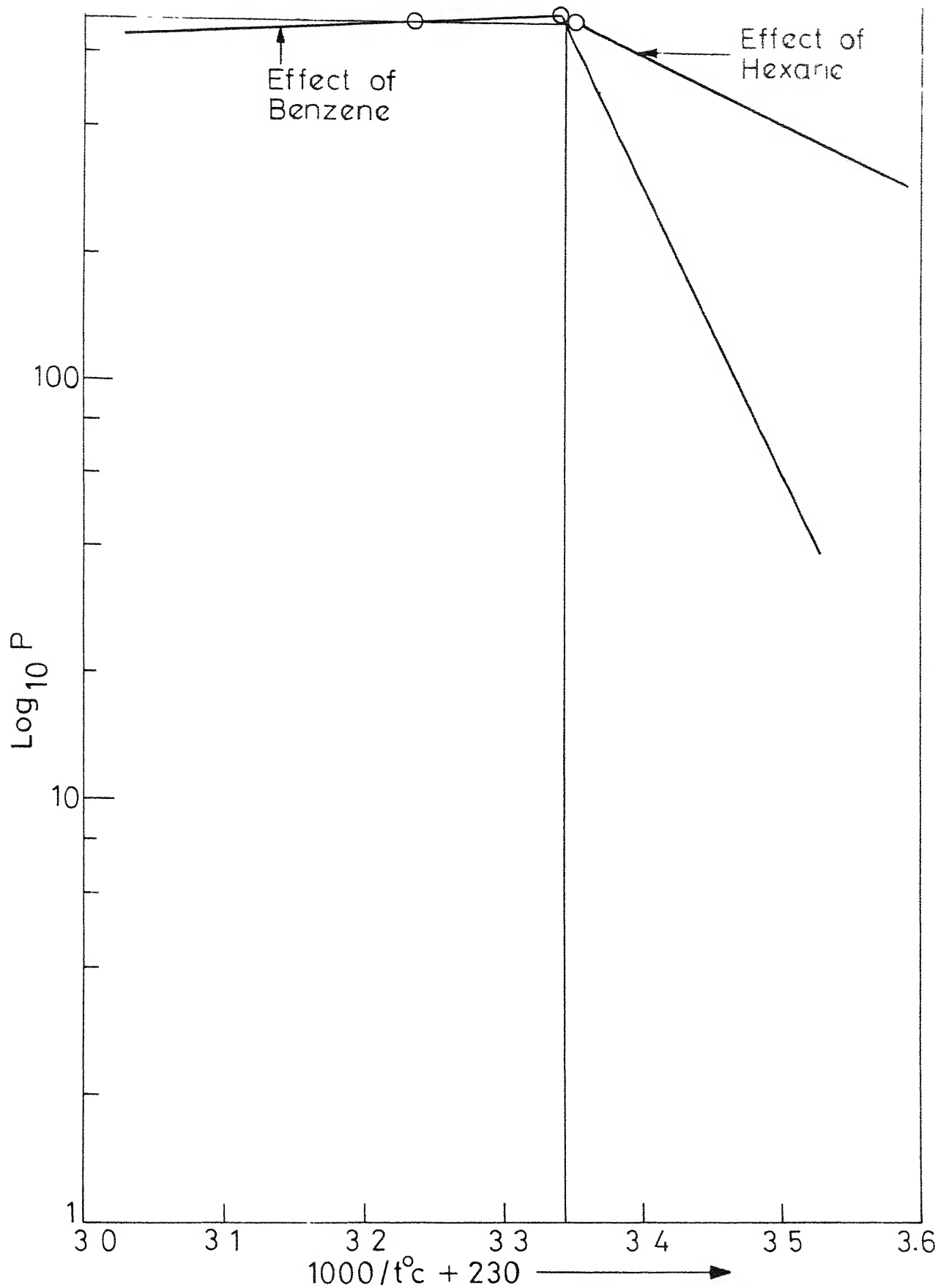


FIG.4.8 APPROXIMATION OF AZEOTROPIC TEMPERATURE FOR SYSTEM BENZENE-CYCLOHEXANE



4.9 APPROXIMATION OF AZEOTROPIC TEMPERATURE FOR SYSTEM HEXANE-BENZENE.

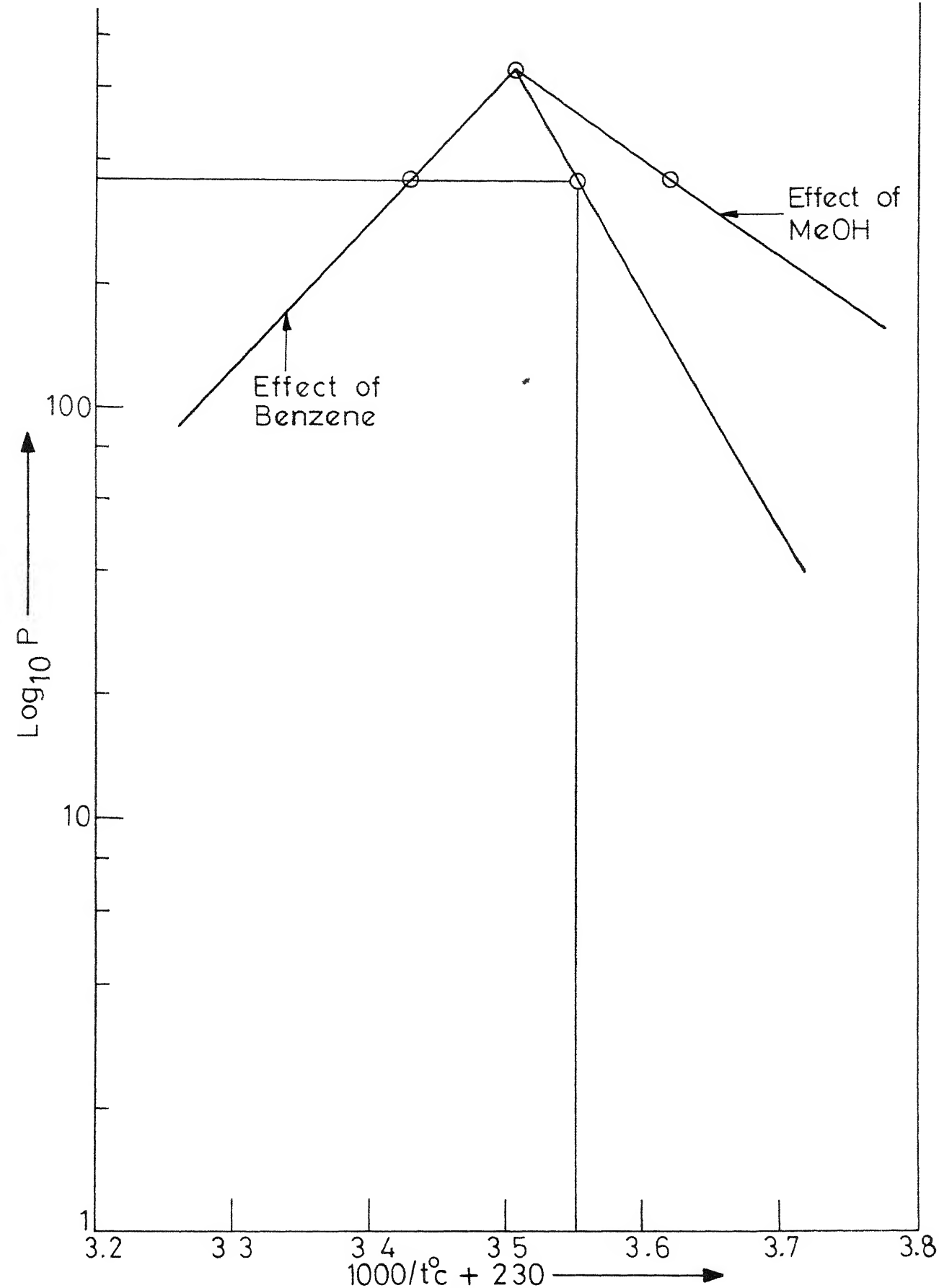


FIG.4.10 APPROXIMATION OF AZEOTROPIC TEMPERATURE FOR SYSTEM METHYL ALCOHOL-BENZENE

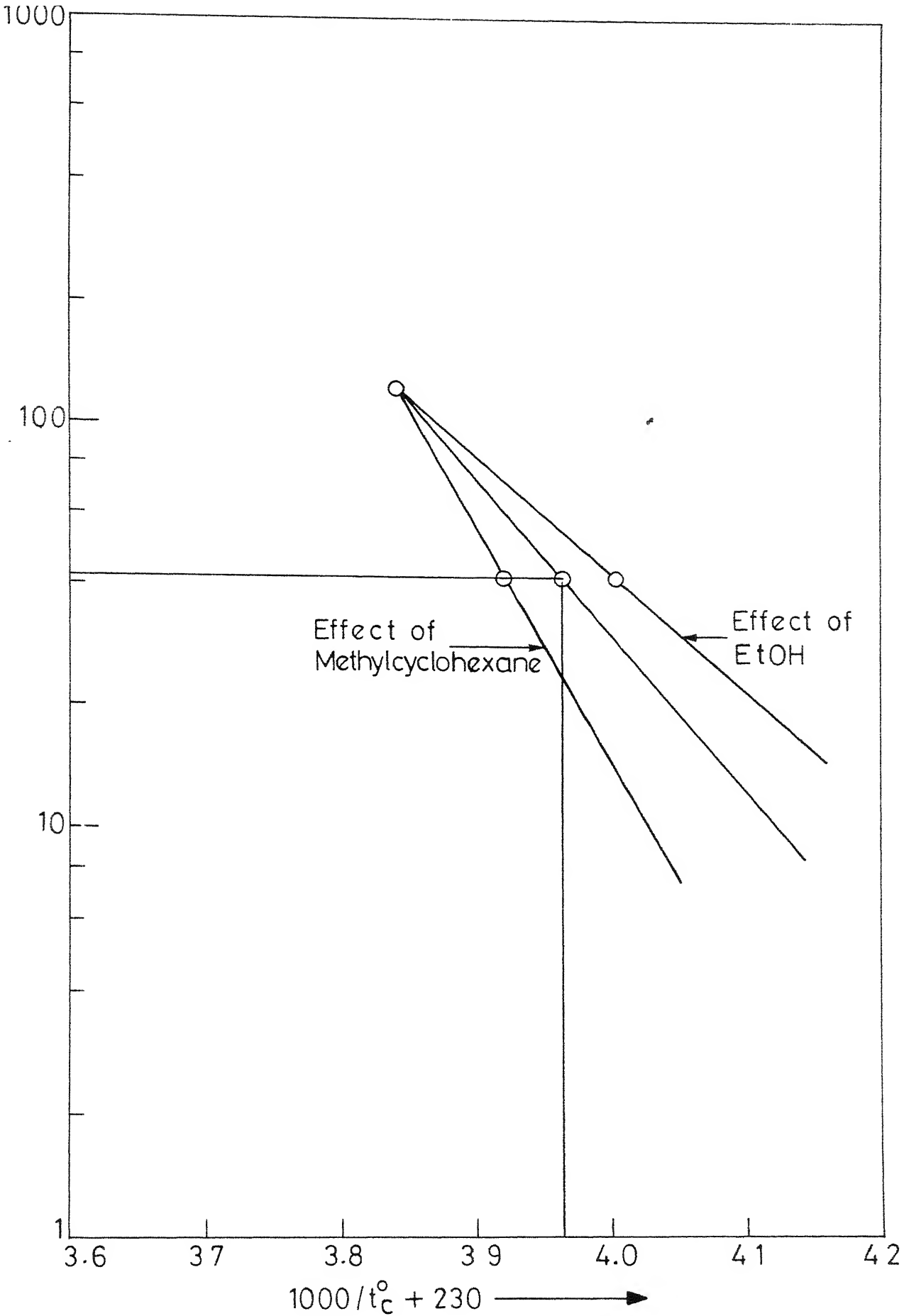


FIG.4.11 APPROXIMATION OF AZEOTROPIC TEMPERATURE

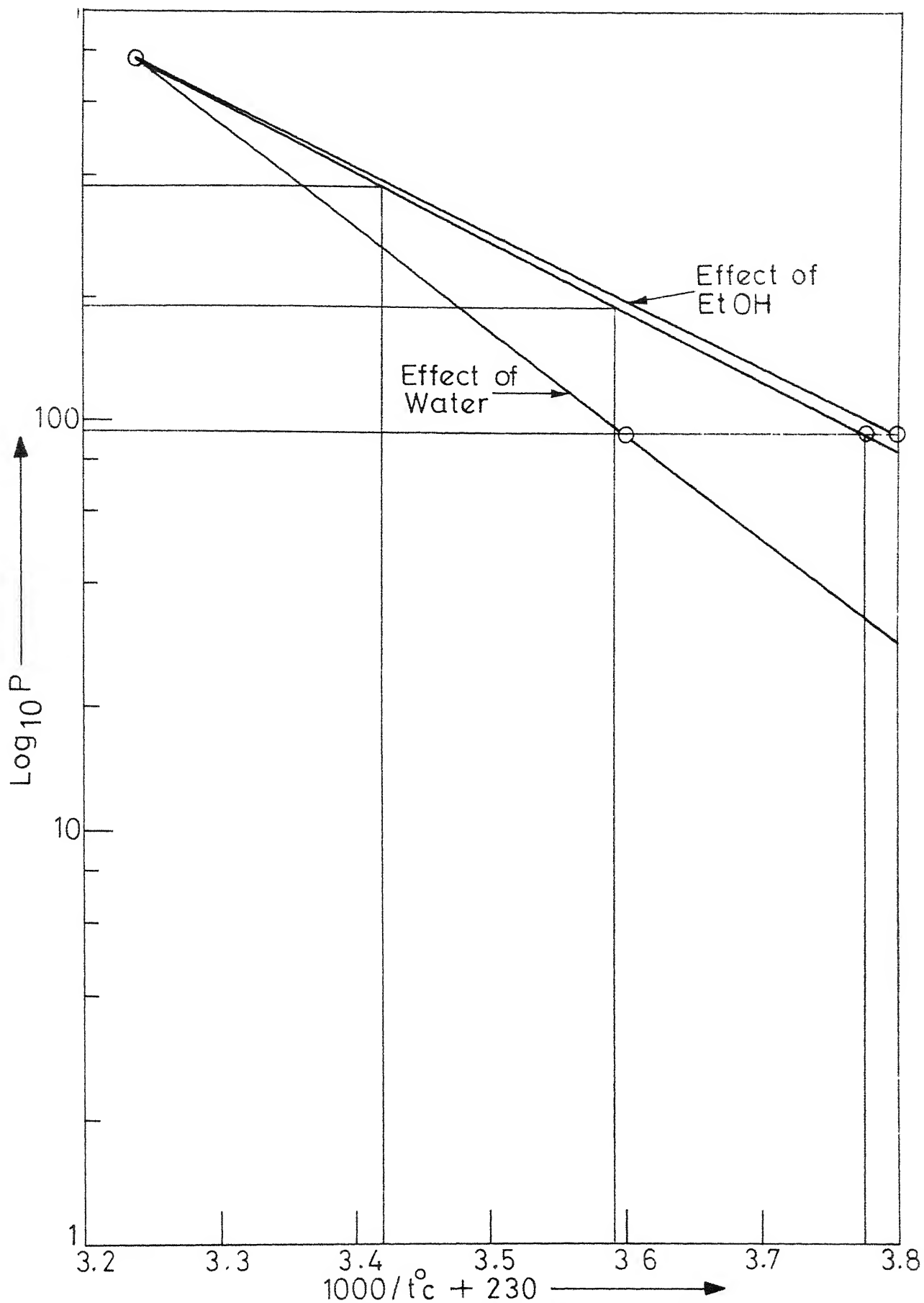


FIG 4.12 APPROXIMATION OF AZEOTROPIC TEMPERATURE FOR SYSTEM. ETHYL ALCOHOL-WATER.

TABLE 7

APPROXIMATION OF AZEOTROPIC TEMPERATURES

Sl. No.	System	Known (P-T-x)	P mm Hg	$T_1, ^\circ\text{K}$	$T_2, ^\circ\text{K}$	$T_{az}(\text{app}) ^\circ\text{K}$
1.	Ethyl alcohol + ethyl acetate	P=760.0 $x_1=0.4610$ $T_{az}=344.96$	423.0 220.0 77.4	337.3 323.0 302.8	333.4 316.8 294.0	333.1 320.1 301.4
2.	Benzene + Cyclohexane	P=759.0 $x_1=0.5020$ $T_{az}=350.56$	600.0 206.0	345.7 316.0	348.2 317.9	349.8 318.6
3.	Hexane + Benzene	P=760.0 $x_1=0.9630$ $T_{az}=341.96$	735.0	340.8	352.1	342.2
4.	Methyl alcohol + Benzene	P=678.4 $x_1=0.6080$ $T_{az}=328.16$	366.0	320.1	331.2	324.8
5.	Ethyl alcohol + Methylcyclohexane	P=120.2 $x_1=0.5400$ $T_{az}=303.16$	41.3	292.1	295.7	295.3
6.	Ethyl alcohol + Water	P=760.0 $x_1=0.8940$ $T_{az}=351.26$	380.0 190.0 95.0 50.0	334.8 320.0 306.6 295.2	354.8 338.4 323.6 311.3	335.5 321.7 308.0 297.8

APPROXIMATION OF AZEOTROPIC RANGE OF COMPOSITION

Sl. No.	System	Known (P-T-x)	F mm Hg.	T_{az} (app)	ΔT_1 (T)	Range of x_1 chosen	ΔT_1 Over the chosen range of x_1
1.	Ethyl alcohol + ethyl acetate	P=760.0 $x_1=0.4610$ $T_{az}=344.9$	423.0 220.0 77.4	333.1 320.1 301.4	1.3991 1.5734 1.8858	0.3500-0.4500 0.2500-0.4000 0.1500-0.3500	1,4481-1.3059 1,6555-1.3908 1,9847-1.5114
2.	Benzene + Cyclohexane	F=759.0 $x_1=0.5020$ $T_{az}=350.5$	600.0 206.0	349.8 318.6	1.0886 1.1240	0.4500-0.5500 0.4000-0.5500	1,1136-1.0611 1,1650-1.0669
3.	Hexane + Benzene	P=760.0 $x_1=0.9630$ $T_{az}=341.9$	735.0	342.2	-	0.0000-1.0000	-
4.	Methyl alcohol + Benzene	P=678.4 $x_1=0.6080$ $T_{az}=328.1$	366.0	324.8	1.3640	0.5500-0.6000	1,4409-1.3298
5.	Ethyl alcohol + Methylcyclohexane	T=120.2 $x_1=0.5400$ $T_{az}=303.1$	41.3	295.3	-	0.0000-1.0000	-
6.	Ethyl alcohol + Water	P=760.0 $x_1=0.8940$ $T_{az}=351.2$	380.0 190.0 95.0 50.0	335.5 321.7 308.0 297.8	- - - -	0.0000-1.0000 0.0000-1.0000 0.0000-1.0000 0.0000-1.0000	- - - -

azeotropic temperatures and compositions (Tables 4 to 6) it is observed that the agreement is very good for all systems excepting the polar-polar mixtures.

The equilibrium liquid and vapor compositions at various predicted azeotropic temperatures have been calculated for all systems and are presented in Table 9. These equilibrium data are plotted in Figure (4.1) to (4.6).

From the analysis of the results it is observed that all the three correlations used for calculation of the excess free energy yield equally good agreement of the predicted azeotropic data with the experimental values, although the inverse temperature dependence of the constants in these correlations may not be valid for highly polar systems.

The first approximation of the azeotropic temperature should be done carefully. This is because equation (3.38) is implicit in T and is highly non-linear so it will have more than one solution. Hence a little off approximation outside a range will result false convergence.

In the Gauss-Seidel iterative method, the convergence is relatively slow. Although fast converging methods such as the Newton-Raphson method are available, all these methods require analytical derivatives of the function used. In the present study the function is quite complicated and hence it is a tedious task to evaluate analytical derivatives of this function.

TABLE 9

EQUILIBRIUM DATA AT DIFFERENT PRESSURES

Sl. No.	System	P mm Hg	T _{az} , °K	x ₁	y ₁
1.	Ethylalcohol + ethylacetate	423.0	329.9	0.3000	0.3335
				0.3500	0.3681
				0.4000	0.3993
				0.4500	0.4280
				0.5000	0.4548
		220.0	314.6	0.2500	0.2758
				0.3000	0.3112
				0.3500	0.3425
				0.4000	0.3707
				0.4500	0.3964
		77.4	293.1	0.1500	0.1700
				0.2000	0.2106
				0.2500	0.2454
				0.3000	0.2756
				0.3500	0.3021
2.	Benzene + cyclohexane	600.0	343.2	0.4000	0.4243
				0.4500	0.4624
				0.5000	0.5004
				0.5500	0.5386
				0.6000	0.5773
		206.0	313.7	0.4000	0.4236
				0.4500	0.4603
				0.5000	0.4969
				0.5500	0.5337
				0.6000	0.5712
3.	Hexane + Benzene	735.0	340.8	0.8500	0.9150
				0.9000	0.9350
				0.9500	0.9550
				0.9700	0.9650
				1.0000	1.0008
4.	Methyl alcohol + Benzene	366.0	313.1	0.5000	0.5773
				0.5500	0.5795
				0.6000	0.5834
				0.6500	0.5896
				0.7000	0.5984

Table 7 (contd)

Sl. No.	System	P mm Hg	T _{az} , °K	x ₁	y ₁
5.	Ethyl alcohol + Methylcyclohexane	41.3	283.3	0.4000	0.5180
				0.4500	0.5046
				0.5000	0.4935
				0.5500	0.4852
				0.6000	0.4804
6.	Ethyl alcohol + Water	380.0	334.7	0.8000	0.8181
				0.8500	0.8569
				0.9000	0.8988
				0.9500	0.9438
				1.0000	0.9919
		190.0	319.8	0.8000	0.8171
				0.8500	0.8554
				0.9000	0.8968
				0.9500	0.9415
				1.0000	0.9894
		95.0	306.3	0.8000	0.8139
				0.8500	0.8514
				0.9000	0.8922
				0.9500	0.9364
				1.0000	0.9840
		50.0	295.0	0.8000	0.8143
				0.8500	0.8513
				0.9000	0.8918
				0.9500	0.9358
				1.0000	0.9832

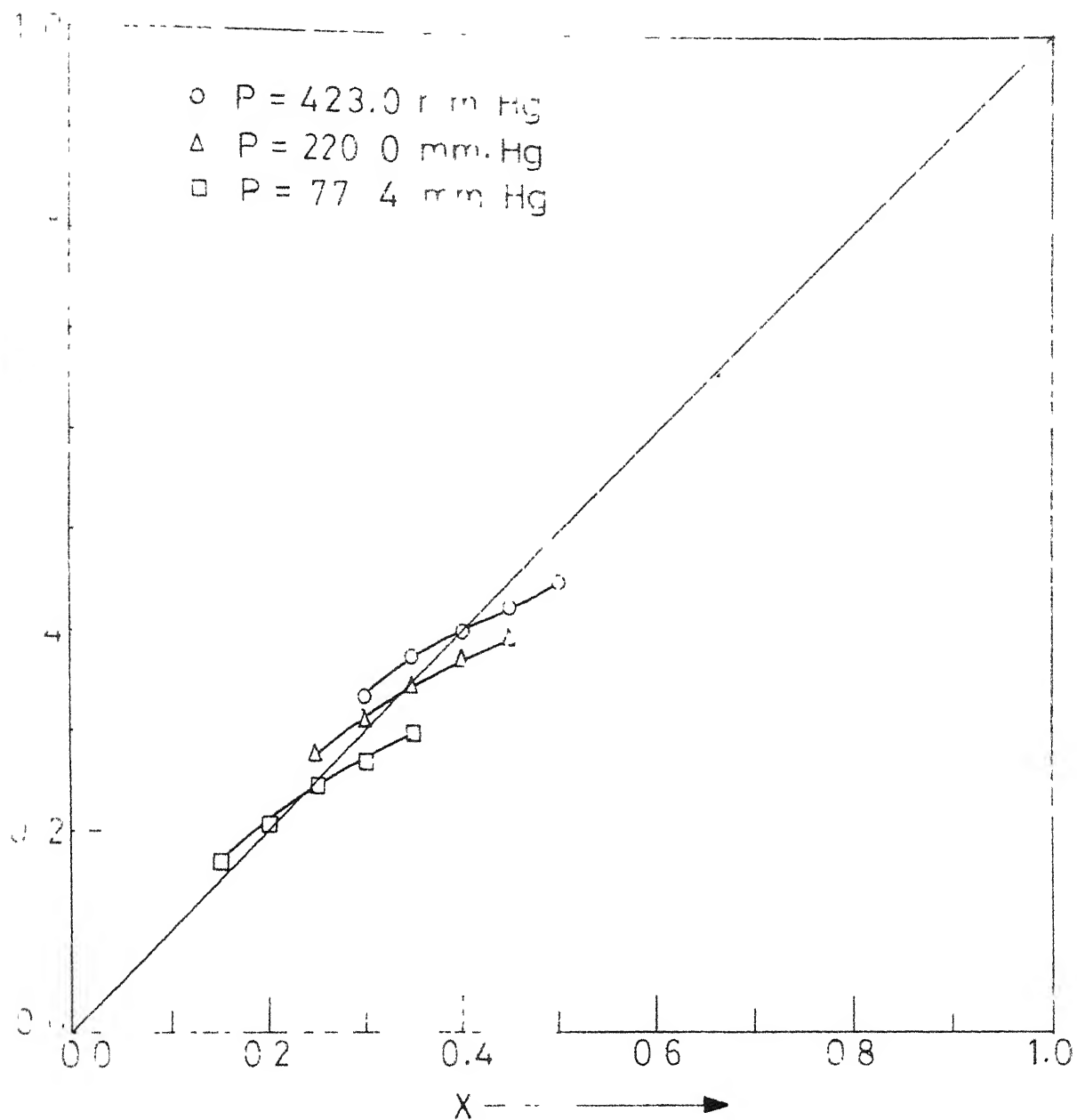


FIG.4.1 EQUILIBRIUM DIAGRAM FOR SYSTEM.
ETHYLALCOHOL-ETHYL ACETATE.

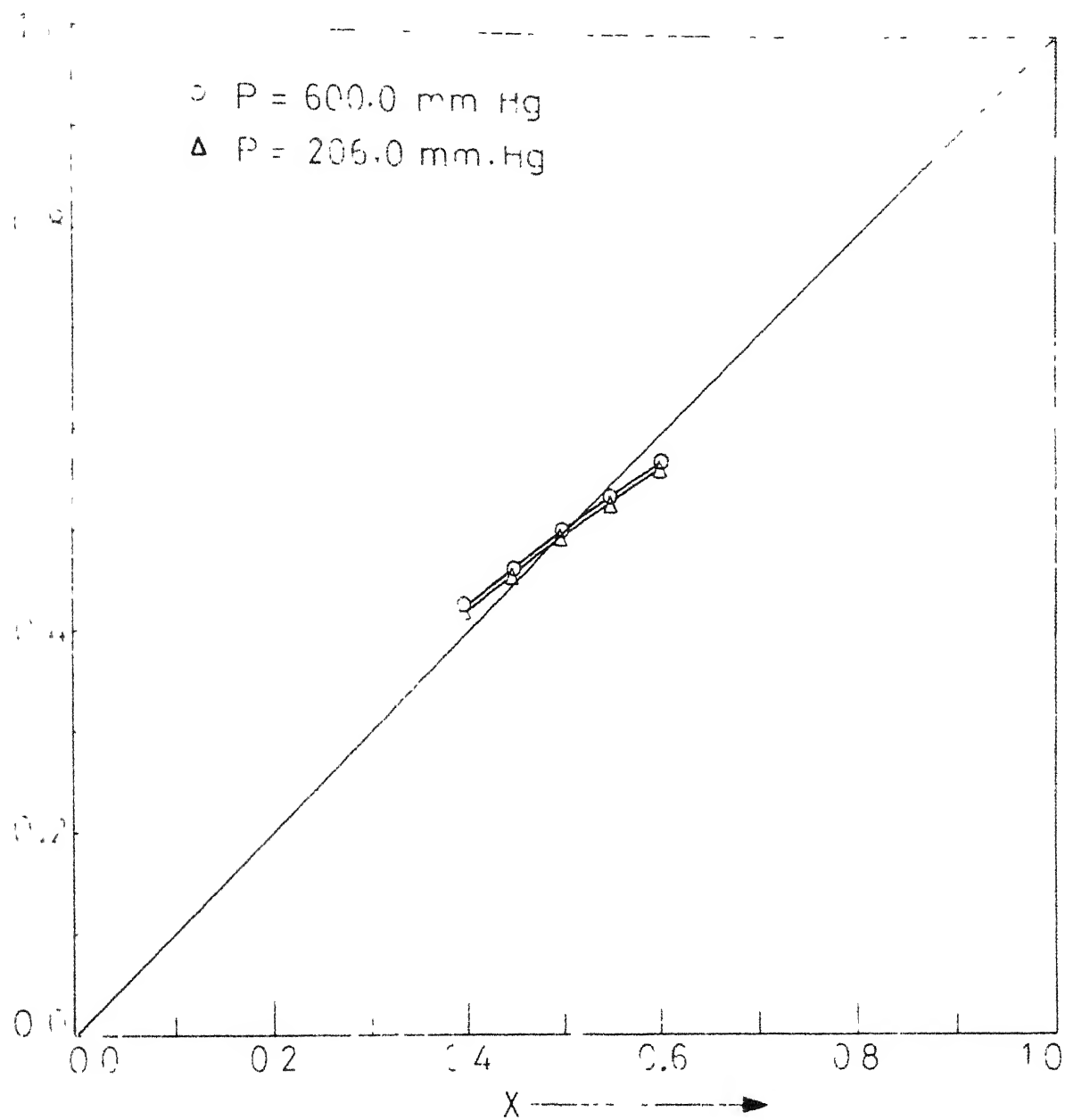


FIG.4 2 EQUILIBRIUM DIAGRAM FOR SYSTEM
BENZENE-CYCLOHEXANE.

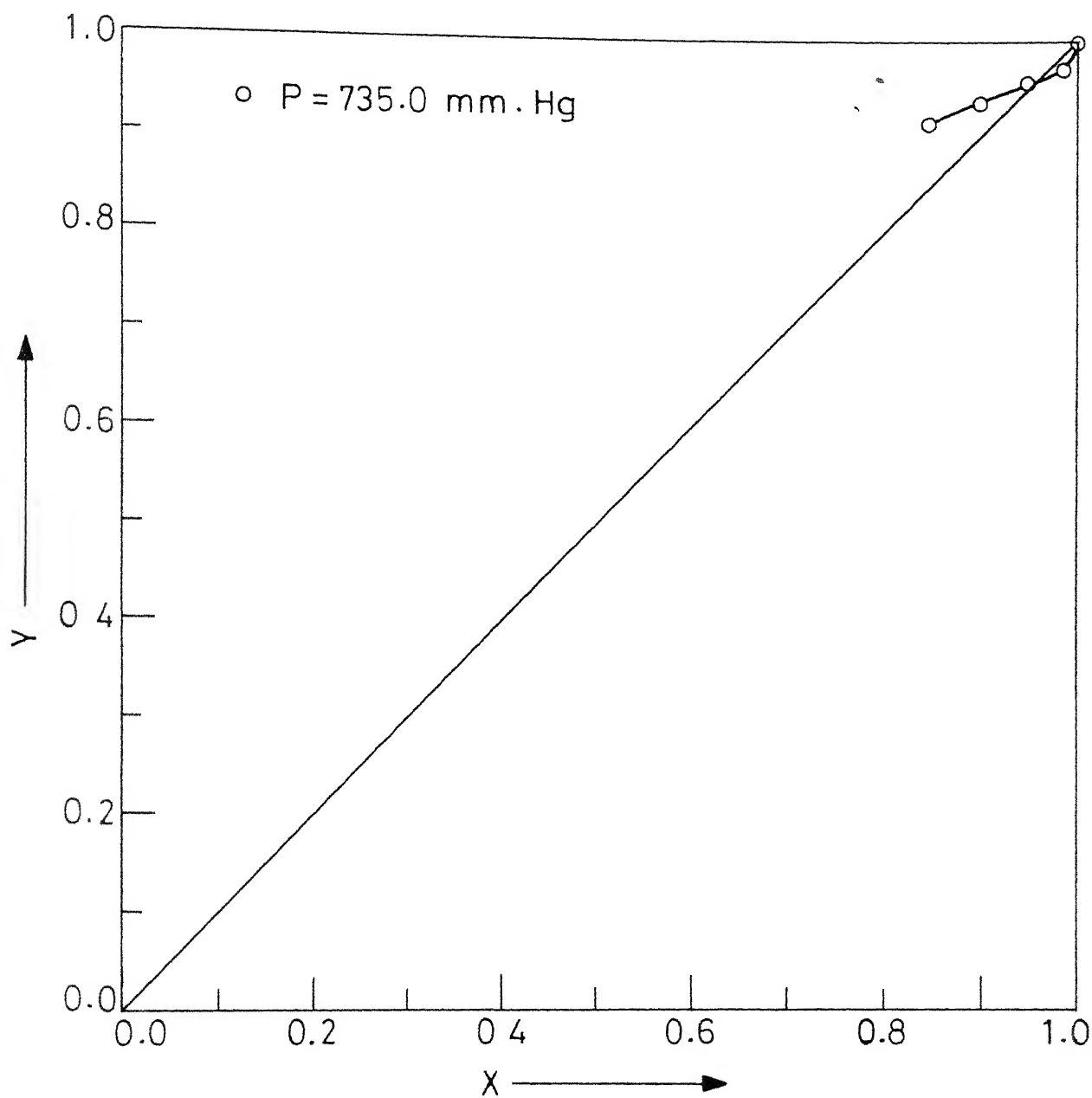


FIG.4.3 EQUILIBRIUM DIAGRAM FOR SYSTEM.
HEXANE - BENZENE.

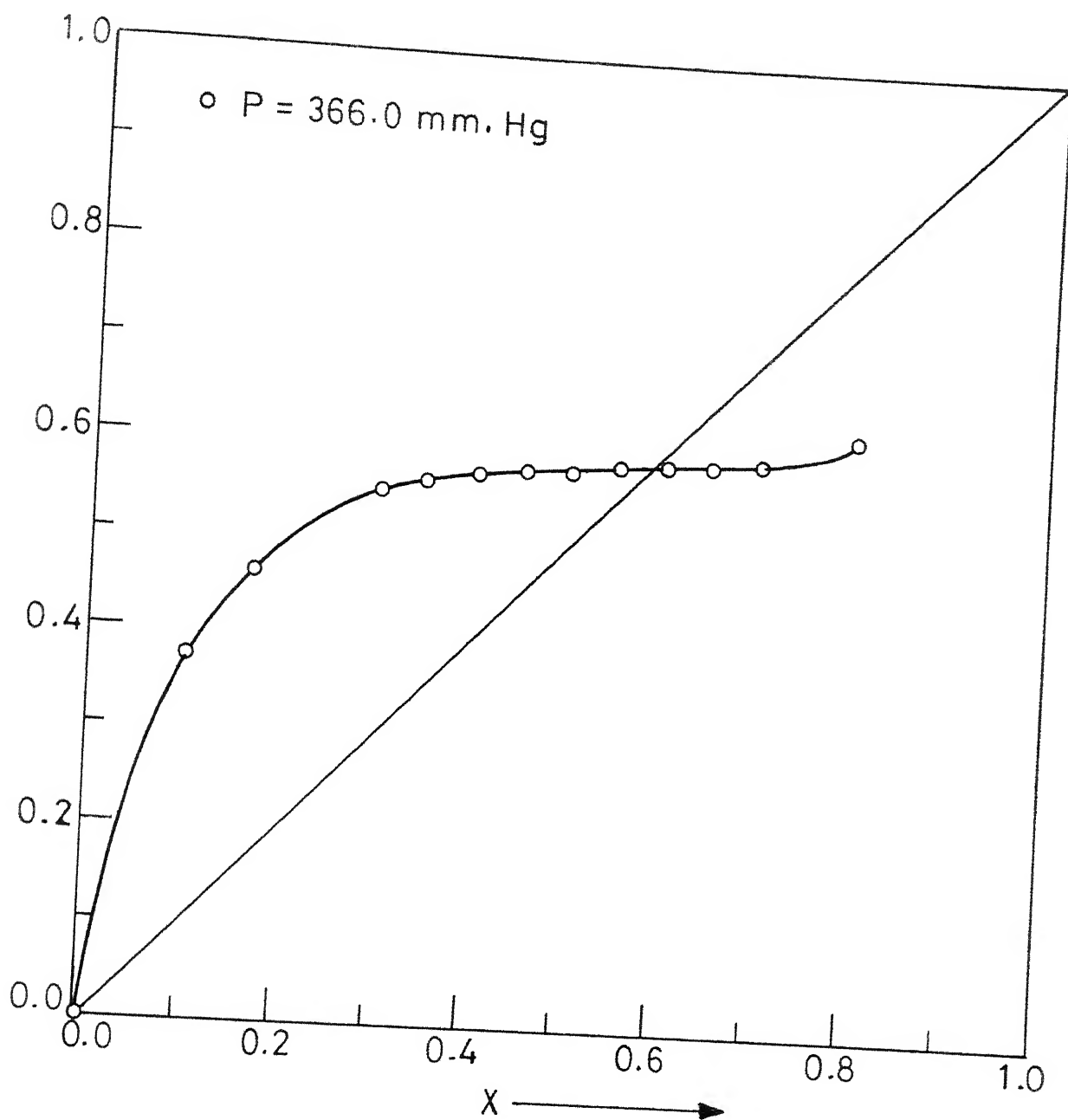


FIG. 4.4 EQUILIBRIUM DIAGRAM FOR SYSTEM.
METHYL ALCOHOL - BENZENE.

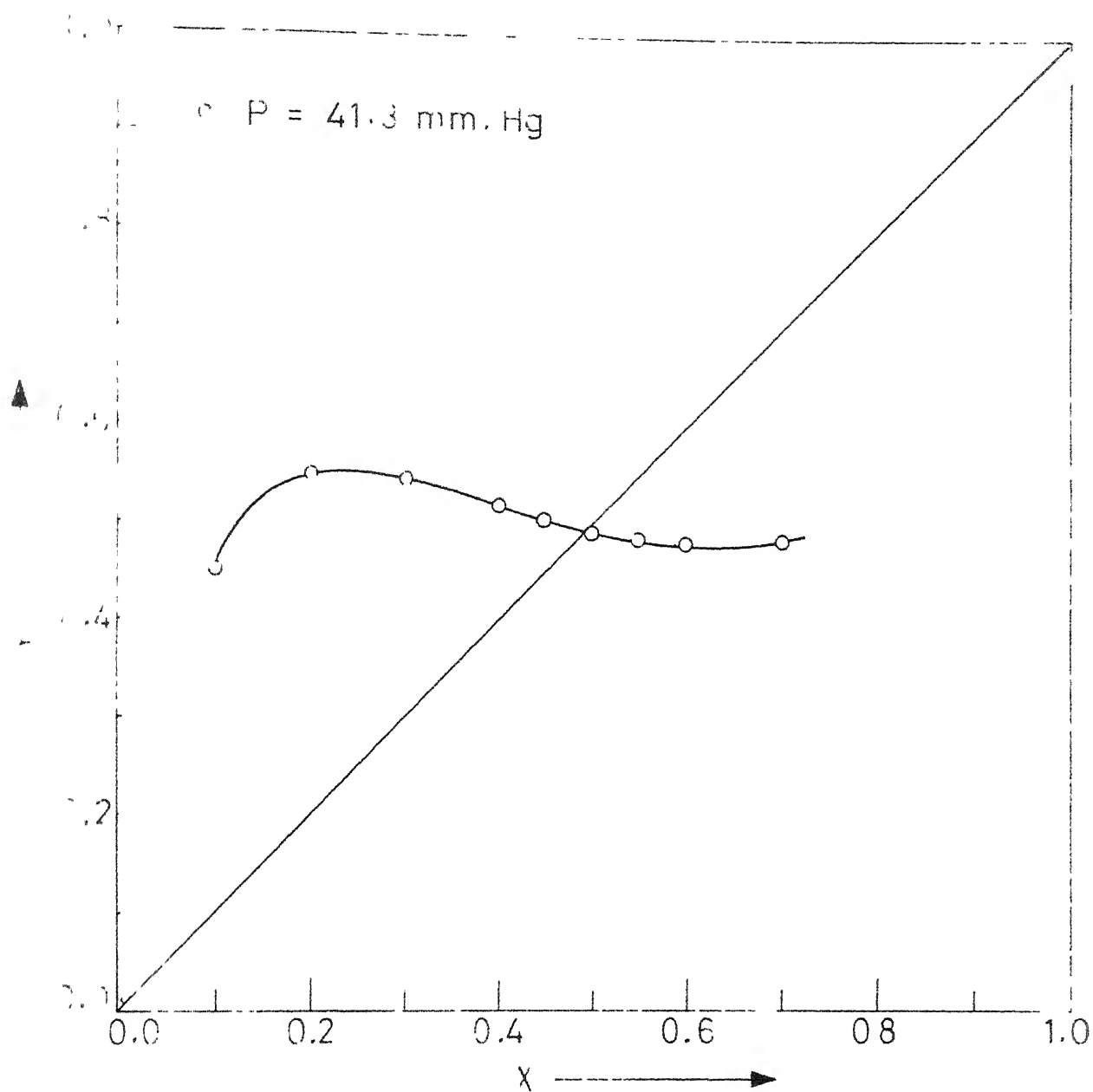


FIG. 4.5 EQUILIBRIUM DIAGRAM FOR SYSTEM. ETHYL ALCOHOL-METHYLCYCLOHEXANE

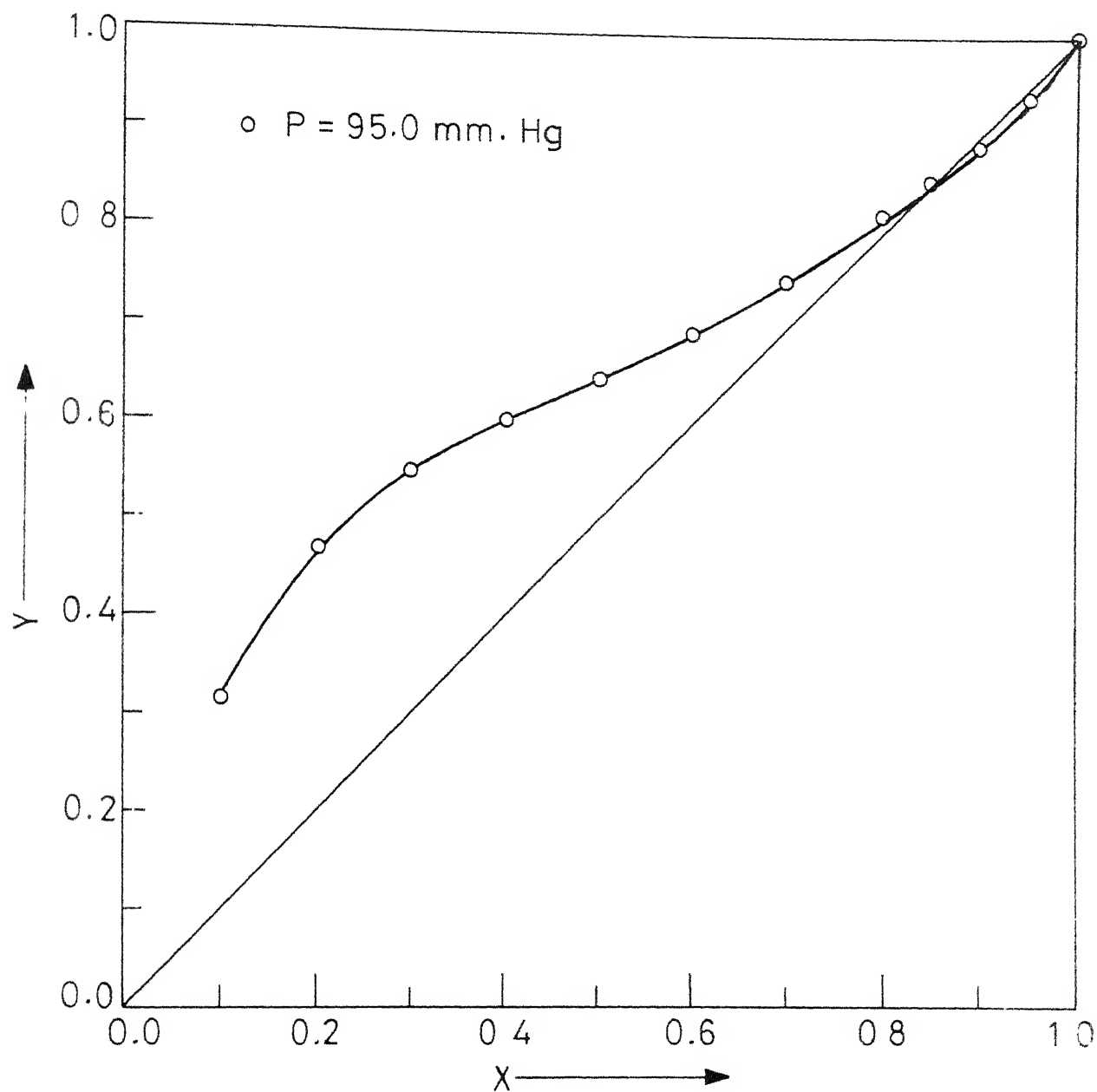


FIG. 4.6 EQUILIBRIUM DIAGRAM FOR SYSTEM
ETHYL ALCOHOL-WATER

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APPENDIX A1. Gauss-Seidel Iterative Method:

Gauss-Seidel iterative scheme is used when the equation is of the form:

$$x = f(x)$$

In the beginning of the iterative scheme initial guess of the value x is necessary. Next in the process of iterations, the newly computed values of x are taken as the next better guess to continue the process. Finally we get the solution when the difference between the newly computed value and the preceding one is negligible.

2. Vapor Pressures, Activity Coefficients, Virial Coefficients and Constants of the Three Equations at Azeotropic Temperature Composition:

Units of P , P_1^0 , P_2^0 - mm of Hg

Units of T_{az} - °K

Units of B_{11} , B_{22} - cc/mole

a. System: Ethyl Alcohol + Ethyl Acetate

$P = 423.0$	$T_{az} = 329.9$	$x_{1az} = 0.3970$
$P_1^0 = 303.35$	$\gamma_1 = 1.3742$	$B_{11} = -2527.5908$
$P_2^0 = 370.30$	$\gamma_2 = 1.1362$	$B_{22} = -1807.5370$
$A_1 = 0.8555$	$A_2 = 0.8245$	$A_3 = 0.8041$
$B_1 = 0.0320$	$B_2 = 0.8889$	$B_3 = 0.8048$

$$\begin{array}{lll}
 P = 220.0 & T_{az} = 314.6 & x_{1az} = 0.3310 \\
 P_1^0 = 144.79 & \gamma_1 = 1.5013 & B_{11} = -3025.6215 \\
 P_2^0 = 200.17 & \gamma_2 = 1.0965 & B_{22} = -2097.4711 \\
 A_1 = 0.8970 & A_2 = 0.8645 & A_3 = 0.8431 \\
 B_1 = 0.0335 & B_2 = 0.9321 & B_3 = 0.8439
 \end{array}$$

$$\begin{array}{lll}
 P = 77.4 & T_{az} = 293.1 & x_{1az} = 0.2390 \\
 P_1^0 = 43.83 & \gamma_1 = 1.7534 & B_{11} = -4047.5522 \\
 P_2^0 = 73.62 & \gamma_2 = 1.0505 & B_{22} = -2658.5524 \\
 A_1 = 0.9629 & A_2 = 0.9280 & A_3 = 0.9050 \\
 B_1 = 0.0360 & B_2 = 1.0005 & B_3 = 0.9058
 \end{array}$$

b. System: Benzene + Cyclohexane

$$\begin{array}{lll}
 P = 600.0 & T_{az} = 343.2 & x_{1az} = 0.4980 \\
 P_1^0 = 551.54 & \gamma_1 = 1.0854 & B_{11} = -1041.8023 \\
 P_2^0 = 508.87 & \gamma_2 = 1.1719 & B_{22} = -1224.4343 \\
 A_1 = 0.4810 & A_2 = 0.7134 & A_3 = 0.6068 \\
 B_1 = -0.1563 & B_2 = 0.3629 & B_3 = 0.2841
 \end{array}$$

$$\begin{array}{lll}
 P = 206.0 & T_{az} = 313.7 & x_{1az} = 0.485 \\
 P_1^0 = 186.75 & \gamma_1 = 1.1018 & B_{11} = -1325.0588 \\
 P_2^0 = 173.88 & \gamma_2 = 1.1811 & B_{22} = -1573.4160 \\
 A_1 = 0.5263 & A_2 = 0.7804 & A_3 = 0.6639 \\
 B_1 = -0.1709 & B_2 = 0.3970 & B_3 = 0.3109
 \end{array}$$

c. System: Hexane + Benzene

$$\begin{array}{lll}
 P = 735.0 & T_{az} = 340.9 & x_{1az} = 0.9610 \\
 P_1^0 = 737.24 & \gamma_1 = 0.9971 & B_{11} = -1339.8401 \\
 P_2^0 = 511.50 & \gamma_2 = 1.4211 & B_{22} = -1059.8589
 \end{array}$$

$$\begin{array}{lll}
 A_1 = 1.2924 & A_2 = -0.0435 & A_3 = 4.8939 \\
 B_1 = -1.0867 & B_2 = 0.2210 & B_3 = 0.2019
 \end{array}$$

d. System: Methylalcohol + Benzene

$$\begin{array}{lll}
 I = 366.0 & T_{az} = 313.1 & x_{1az} = 0.5800 \\
 P_1^0 = 265.26 & \gamma_1 = 1.3705 & B_{11} = -1597.3142 \\
 P_2^0 = 182.49 & \gamma_2 = 1.9730 & B_{22} = -1331.6952 \\
 A_1 = 1.9401 & A_2 = 2.0634 & A_3 = 1.7668 \\
 B_1 = -0.1127 & B_2 = 1.8313 & B_3 = 1.3029
 \end{array}$$

e. System: Ethylalcohol + Methyl Cyclohexane

$$\begin{array}{lll}
 P = 41.3 & T_{az} = 283.3 & x_{1az} = 0.4935 \\
 P_1^0 = 23.65 & \gamma_1 = 1.7382 & B_{11} = -4704.6868 \\
 P_2^0 = 21.59 & \gamma_2 = 1.9059 & B_{22} = -2854.3253 \\
 A_1 = 2.3952 & A_2 = 2.6756 & A_3 = 2.3053 \\
 B_1 = -0.2467 & B_{22} = 2.1683 & B_3 = 1.1315
 \end{array}$$

f. System: Ethylalcohol + Water

$$\begin{array}{lll}
 P = 380.0 & T_{az} = 334.7 & x_{1az} = 0.8800 \\
 P_1^0 = 376.06 & \gamma_1 = 1.0101 & B_{11} = -2398.6809 \\
 P_2^0 = 160.24 & \gamma_2 = 2.3409 & B_{22} = -1115.1555 \\
 A_1 = 1.2022 & A_2 = 1.5880 & A_3 = 0.0700 \\
 B_1 = -0.1999 & B_2 = 1.0040 & B_3 = 1.0027
 \end{array}$$

$$\begin{array}{lll}
 P = 190.0 & T_{az} = 319.8 & x_{1az} = 0.8735 \\
 P_1^0 = 187.73 & \gamma_1 = 1.0119 & B_{11} = -2840.3379 \\
 P_2^0 = 78.08 & \gamma_2 = 2.4137 & B_{22} = -1288.5237 \\
 A_1 = 1.2582 & A_2 = 1.6619 & A_3 = 0.0733 \\
 B_1 = -0.2092 & B_2 = 1.0507 & B_3 = 1.0494
 \end{array}$$

$$\begin{array}{lll}
 P = 95.0 & T_{az} = 306.3 & x_{1az} = 0.8670 \\
 P_1^0 = 93.69 & \gamma_1 = 1.0139 & B_{11} = -3363.7714 \\
 P_2^0 = 38.02 & \gamma_2 = 2.4844 & B_{22} = -1489.6359 \\
 A_1 = 1.3133 & A_2 = 1.7347 & A_3 = 0.0765 \\
 B_1 = -0.2184 & B_2 = 1.0968 & B_3 = 1.0954
 \end{array}$$

$$\begin{array}{lll}
 P = 50.0 & T_{az} = 295.0 & x_{1az} = 0.8610 \\
 P_1^0 = 49.22 & \gamma_1 = 1.0157 & B_{11} = -3934.7287 \\
 P_2^0 = 19.52 & \gamma_2 = 2.5522 & B_{22} = -1704.7313 \\
 A_1 = 1.3637 & A_2 = 1.8013 & A_3 = 0.0794 \\
 B_1 = -0.2267 & B_2 = 1.1389 & B_3 = 1.1374
 \end{array}$$

APPENDIX B

COMPUTER PROGRAM

LIST OF IMPORTANT VARIABLES USED IN COMPUTER PROGRAMS ONE THROUGH THREE

VL1,VL2	MOLAR VOLUME OF PURE COMPONENTS (LIQUID) ONE AND TWO.
RHO,RHOC,S,VOSTAR	KREGLESKI S CONSTANTS
A1,B1,C1	ANTOINE CONSTANTS FOR COMPONENT ONE
A2,B2,C2	ANTOINE CONSTANTS FOR COMPONENTS TWO
VSTAR	LIQUID MOLAR VOLUME AT REDUCED TEMPERATURE $T/T_C=0.6$
ESTAR	ENERGY OF VAPORIZATION OF COMPONENT AT REDUCED TEMP.
TC	CRITICAL TEMPERATURE
TO,X1,X2,P	OBSERVED AZEOTROPIC TEMP., COMPOSITION AND PRESSURE
T1,T2	BOILING POINTS OF PURE COMPONENTS IN MIXTURE IN K
VC(1,1)	VIRIAL COEFFICIENT OF PURE COMPONENT ONE
VC(2,2)	VIRIAL COEFFICIENT OF PURE COMPONENT TWO
VC(1,2)	INTERACTION VIRIAL COEFFICIENT OF THE MIXTURE
GAMA1	ACTIVITY COEFFICIENT OF COMPONENT ONE
GAMA2	ACTIVITY COEFFICIENT OF COMPONENT TWO
AT(M)	APPROXIMATE TEMPERATURE EVALUATED
GE	EXCESS GIBBS FREE ENERGY
VP1,VP2	VAPOR PRESSURES OF COMPONENTS ONE AND TWO
B	PACKING FACTOR
RKA,RKB	REDLICH-KISTER CONSTANTS
VLA,VLB	VAN-LAAR CONSTANTS
SHA,SHB	SCATCHARD-HAMMER CONSTANTS

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*
* PROGRAM T *
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PREDICTION OF AZEOTROPIC BOILING TEMPERATURES, USING REDLICH-KISTER,
VAN-LAAR AND SCATCHARD-HAMMER EQUATIONS.

C LIQUID MOLAR VOLUMES ARE ASSUMED TO BE INDEPENDENT OF TEMP. AND PRE.
C FOR CALCULATION OF VIRIAL COEFFICIENTS KREGLESKI'S METHOD IS USED
C FOR VAPOR PRESSURE CALCULATION ANTOINE EQUATION IS USED
C UNITS OF R (MM OF HG)(C.C.)/(GM-MOLE)(K)

```

      DIMENSION U(10),VC(10,10),VSTAP(5),ESTAR(5),TC(5),AT(100),UU(20)
      VL1=46.07/0.789
      VL2=88.01/0.901
      R=80.06*760.
1   FORMAT(/,15X,*R-K CONSTANTS*,//,6X,*GAMA1*,7X,*GAMA2*,9X,*RKA*,10X,
1,*RKB*,10X,*T1*,11X,*T2*,/)
2000  FORMAT(/,2F14.4,3F16.4,F15.4)
2   FORMAT(/,15X,*VAN-LAAR CONSTANTS*,//,6X,*GAMA1*,7X,*GAMA2*,9X,*VL1*,
1,*VL2*,10X,*T1*,11X,*T2*,/)
103  FORMAT(/,15X,*SCATCHARD-HAMMER CONSTANTS*,//,6X,*GAMA1*,7X,*GAMA2*,
1,*SHA*,10X,*SHB*,10X,*T1*,11X,*T2*,/)
3   FORMAT(1H1,/,10X,*COMPARISON OF OBSERVED AND PREDICTED TEMPERATURES BY R-K,VAN-LAAR AND SCATCHARD HAMMER EQUATIONS*,//)
5   FORMAT(/,15X,*FOR ETHANOL*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*DELTA*,8X,*
1VC(1,2)*,/)
8   FORMAT(/,15X,*FOR BENZENE*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*DELTA*,8X,*
1VC(1,2)*,/)
320  FORMAT(/,15X,*FOR HEXANE*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*DELTA*,8X,*
1VC(1,2)*,/)
321  FORMAT(/,15X,*FOR METHANOL*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*DELTA*,8X,*
1VC(1,2)*,/)
322  FORMAT(/,15X,*FOR METHYLCYCLOPENTANE*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*
1DELTA*,8X,*VC(1,2)*,/)
6   FORMAT(/,15X,*FOR ETHYL ACETATE*,/,8X,*VP2*,9X,*VC(2,2)*,7X,*DELTA*,
1*,8X,*VC(1,2)*,/)
11  FORMAT(/,15X,*FOR CYCLOHEXANE*,/,8X,*VP2*,9X,*VC(2,2)*,7X,*DELTA*,
1*,8X,*VC(1,2)*,/)
323  FORMAT(/,15X,*FOR METHYLCYCLOHEXANE*,/,8X,*VP2*,9X,*VC(2,2)*,7X,*
1DELTA*,8X,*VC(1,2)*,/)

```

```

1000 FORMAT(/,15X,*FOR BENZENE*,/,8Y,*VP2*,9X,*VC(2,2)*,7X,*DELTA*,8Y,*
1VC(1,2)*,/)
7  FORMAT(4F16.1,/)
22  FORMAT(1H1,/,50X,*SYSTEM- ETHYL ALCOHOL AND ETHYL ACETATE*,/,50Y,2
19(1H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7
2.4,2X,*X2=*,F7.4,/)
33  FORMAT(1H1,/,50X,*SYSTEM- BENZENE AND CYCLOHEXANE*,/,50Y,21(1H*),/
1/,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4,2X,*Y
22=*,F7.4,/)
314 FORMAT(1H1,/,50X,*SYSTEM- HEXANE AND BENZENE*,/,50X,26(1H*),//,5X,
1*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4,2X,*X2=*,F
27.4,/)
316 FORMAT(1H1,/,50X,*SYSTEM- METHANOL AND BENZENE*,/,50X,20(1H*),//,5
1X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4,2X,*X2=*,F
27.4,/)
318 FORMAT(1H1,/,50X,*SYSTEM- METHYLCYCLOPENTANE AND BENZENE*,/,50X,20
1(1H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.
24,2X,*X2=*,F7.4,/)
319 FORMAT(1H1,/,50X,*SYSTEM- ETHANOL AND METHYLCYCLOHEXANE*,/,50X,27(
11H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4
2,2X,*X2=*,F7.4,/)
77  FORMAT(/,5X,F7.4,5X,F7.4,5X,F9.4,5X,F8.4,5X,F8.2,5X,F8.2,/)
99  FORMAT(F4.1,F5.3,F5.3,F6.1)
222 FORMAT(F3.1,F4.2,F4.2,F4.2,F5.2,F6.2,F6.2,F6.2)
109 FORMAT(F7.5,F8.3,F7.3,F7.5,F8.2,F7.3)
666 FORMAT(F5.3,F7.1,F6.2)
66  FORMAT(/,5X,F8.2,5X,F9.2,5X,F8.2,5X,F9.2,5X,F9.4,/)
4   FORMAT(/,5X,*CHECK POINT*,5X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4
1,2X,*X2=*,F7.4,/)
104 FORMAT(/,2X,*APPROXIMATE TEMPERATURE EVALUATED=*,F8.2,/)
88  FORMAT(/,9X,*CBS TEMP*,10X,*RKTE*,12X,*VLTE*,12X,*SHTE*,/)
DO600MP=1,6
N=1
MN=0
IN=0
MA=0
MM=1
READ222,F,RHO,RHOC,S,VOSTAR,RKT,VLT,SHT
READ109,A1,B1,C1,A2,B2,C2
DO333 II=1,2
READ666,VSTAR(II),ESTAR(II),TC(II)
333 CONTINUE
IF(MP.EQ.1)MQ=6
IF(MP.EQ.2)MQ=4
IF(MP.EQ.3)MQ=2
IF(MP.EQ.4)MQ=2
IF(MP.EQ.5)MQ=3
IF(MP.EQ.6)MQ=2
DO2COM=1,MQ
DIFMIN=100.

```

```

JJ=0
NN=0
READ99,TO,X1,X2,P
UU(M)=TO+273.16
T1=B1*(1./((A1-ALOG(P)/2.303))-C1+273.16
T2=B2*(1./((A2-ALOG(P)/2.303))-C2+273.16
U(M)=TO+273.16
IF(N-1)10,10,100
10 DO400 I=1,2
   CALL VIRIAL(U,RHO,S,VOSTAR,VSTAR,ESTAR,VC,TC,M,I)
400 CONTINUE
   DELTA=2.*VC(1,2)-VC(1,1)-VC(2,2)
   T=TC
   CALL VPC(T,A1,B1,C1,A2,B2,C2,VP1,VP2)
   IF(MP.EQ.1)PRINT22,P,TO,X1,X2
   IF(MP.EQ.1)GOTO44
101 VL1=78./0.879
   VL2=84./0.779
   IF(MP.EQ.2)PRINT33,P,TO,X1,X2
   IF(MP.EQ.2)GOTO44
   VL1=86./0.65937
   VL2=78./0.879
   IF(MP.EQ.3)PRINT314,P,TO,X1,X2
   IF(MP.EQ.3)GOTO44
   VL1=32./0.7924
   VL2=78./0.879
   IF(MP.EQ.4)PRINT316,P,TO,X1,X2
   IF(MP.EQ.4)GOTO44
   VL1=84./0.750
   VL2=78./0.879
   IF(MP.EQ.5)PRINT318,P,TO,X1,X2
   IF(MP.EQ.5)GOTO44
   VL1=46.07/0.789
   VL2=98./0.769
   IF(MP.EQ.6)PRINT319,P,TO,X1,X2
44  AA=ALOG(P/VP1)
   BB=F/(R*U(M))
   CC=(VC(1,1)-VL1)*(P-VP1)
   DD=P*DELTA*X2*X2
   IF(MP.EQ.1)PRINT5
   IF(MP.EQ.2)PRINT8
   IF(MP.EQ.3)PRINT320
   IF(MP.EQ.4)PRINT321
   IF(MP.EQ.5)PRINT322
   IF(MP.EQ.6)PRINT5
   PRINT66,VP1,VC(1,1),DELTA,VC(1,2),VL1
   AAA=ALOG(P/VP2)
   BBB=F/(R*U(M))
   CCC=(VC(2,2)-VL2)*(P-VP2)
   DDD=P*DELTA*X1*X1

```

```

IF(MP.EQ.1)PRINT6
IF(MP.EQ.2)PRINT11
IF(MP.EQ.3)PRINT1000
IF(MP.EQ.4)PRINT1000
IF(MP.EQ.5)PRINT1000
IF(MP.EQ.6)PRINT1000
PRINT66,VP2,VC(2,2),DELTA,VC(1,2),VL2
GAMA1=EXP(ALOG(P/VP1)+(F/(R*U(M)))*((VC(1,1)-VL1)*(P-VP1)+P*DELTA^
1*X2*X2))
GAMA2=EXP(ALOG(P/VP2)+(F/(R*U(M)))*((VC(2,2)-VL2)*(P-VP2)+P*DELTA^
1*X1*X1))
CALL RK(GAMA1,GAMA2,X1,X2,MN,RKA,RKB,GE,R,AT,M)
PRINT1
PRINT77,GAMA1,GAMA2,RKA,RKB,T1,T2
CALL VANLAR(IN,GAMA1,GAMA2,X1,X2,VLA,VLB,GE,R,AT,M)
PRINT2
PRINT77,GAMA1,GAMA2,VLA,VLB,T1,T2
CALL SCAHAM (GAMA1,GAMA2,X1,X2,MA,SHA,SHB,GE,R,AT,M,VL1,VL2)
PRINT103
PRINT77,GAMA1,GAMA2,SHA,SHB,T1,T2
N=N+1
PRINT3
GOTO 200
100 AT(M)=T1*X1+T2*X2
PRINT4,P,TO,X1,X2
PRINT104,AT(M)
PRINT88
AT(M-1)=RKT
555 RKA=RKA*AT(M-1)/AT(M)
RKB=RKB*AT(M-1)/AT(M)
AT(M-1)=AT(M)
RKT=AT(M)
ZZ1=RKA
ZZ2=RKB
CALL RK(GAMA1,GAMA2,X1,X2,MN,RKA,RKB,GE,R,AT,M)
444 U(M)=AT(M)
DO500 I=1,2
CALL VIRIAL(U,RHO,S,VOSTAR,VSTAR,ESTAR,VC,TC,M,I)
500 CONTINUE
DELTA=2.*VC(1,2)-VC(1,1)-VC(2,2)
T=AT(M)-273.16
CALL VPC(T,A1,B1,C1,A2,B2,C2,VP1,VP2)
V1=((VL1-VC(1,1))*(P-VP1)-DELTA*X2*X2*P)/(R*AT(M))
V2=((VL2-VC(2,2))*(P-VP2)-DELTA*X1*X1*P)/(R*AT(M))
V=X1*V1+X2*V2
DELS1=R*AT(M)*ALOG(P/VP1)/(T1-AT(M))
DELS2=R*AT(M)*ALOG(P/VP2)/(T2-AT(M))
DELSO=X1*DELS1+X2*DELS2
AT1=T1*X1*DELS1/DELSO
AT2=T2*X2*DELS2/DELSO

```

```

AT3=GE/DELSO
AT4=R*AT(M)*V/DELSO
AT(M)=AT1+AT2-AT3-AT4
BT=AT(M)-273.16
DIFF=ABS(BT-TQ)
IF(DIFF.LT.DIFMIN)GOTO111
1004 IF(NN-1)300,700,1001
111 EE=AT(M)
OP=VC(1,1)
OQ=VC(2,2)
OR=VC(1,2)
OS=DELTA
DIFMIN=DIFF
IF(JJ-1)555,55,102
300 RKTE=EE
OT=CP
OU=CQ
OV=CR
OX=CS
AT(M)=T1*X1+T2*X2
AT(M-1)=VLT
DIFMIN=100.
JJ=JJ+1
MM=MM+1
NN=NN+1
55 VLA=VLA*AT(M-1)/AT(M)
VLB=VLB*AT(M-1)/AT(M)
AT(M-1)=AT(M)
VLT=AT(M)
ZZ1=VLA
ZZ2=VLB
CALL VANLAR(IN,GAMA1,GAMA2,X1,Y2,VLA,VLB,GE,R,AT,M)
GOTC 444
700 VLTE=EE
PT=CP
PU=CQ
PV=CR
PX=CS
AT(M)=T1*X1+T2*X2
AT(M-1)=SHT
DIFMIN=100.
JJ=JJ+1
NN=NN+1
102 SHA=SHA*AT(M-1)/AT(M)
SHB=SHB*AT(M-1)/AT(M)
AT(M-1)=AT(M)
SHT=AT(M)
SHT E=EE
QT=CP
QU=CQ

```



```

QV=CR
QX=CS
ZZ1=SHA
ZZ2=SHB
CALL SCAHAM (GAMA1,GAMA2,X1,X2,MA,SHA,SHB,GE,R,AT,M,VL1,VL2)
GOTC444
1001 PRINT7,UU(M),RKTE,VLTE,SHTF
      PRINT2000,RKA,RKB,DT,OU,OV,OX
      PRINT2000,VLA,VLB,PT,PU,PV,PX
      PRINT2000,SHA,SHB,QT,QU,QV,QX
200  CONTINUE
600  CONTINUE
      PRINT9
      9  FORMAT(1H1)
      STOP
      END
C  THIS SUBROUTINE CALCULATES THE VAPOUR PRESSURES OF THE COMPONENTS
      SUBROUTINE VPC(T,A1,B1,C1,A2,B2,C2,VP1,VP2)
      VP1=EXP(2.303*(A1-B1/(T+C1)))
      VP2=EXP(2.303*(A2-B2/(T+C2)))
      RETURN
      END
C  THIS SUBROUTINE CALCULATES THE VIRIAL COEFFICIENTS
      SUBROUTINE VIRIAL(U,RHO,S,VOSTAR,VSTAR,ESTAR,VC,TC,M,I)
      DIMENSION U(10),VC(10,10),VSTAR(5),ESTAR(5),TC(5)
      J=2
      B=0.77+0.1325*(TC(I))**(0.334)
      R1=(1.+S/(VSTAR(I)))*3
      R2=(1.+VOSTAR/(VSTAR(I)))*3
      R=1.987
C  UNITS OF R - G.CAL,C.C./GM.-MOLE,OK
      RP1=(RHO*ESTAR(I)*0.239)/(R*U(M))
      RP2=S*RP1
      WSTAR=VSTAR(I)*3
      VC(I,I)=B*WSTAR*(1.-(R1-1.)*(EXP(RP1)-1.)-(R2-R1)*(EXP(RP2)-1.))
      IF(I.LT.2)GOTO999
      VC(I-1,J)=(2.*VC(I-1,I-1)*VC(I,I))/(VC(I,I)+VC(I-1,I-1))
999  RETURN
      END
C  THIS SUBROUTINE IS FOR REDLICH-KISTER EQUATION
      SUBROUTINE RK(GAMA1,GAMA2,X1,X2,MN,RKA,RKB,GE,R,AT,M)
      DIMENSION AT(100)
      MN=MN+1
      IF(MN.GT.1)GOTO50
      B1=X2*X2
      C1=(X1*X1*X2+5.*X1*X2*X2-X2)
      B2=X1*X1
      C2=(X1-X1*X2*X2-5.*X1*X1*X2)
      RKB=((ALOG(GAMA1)/B1)-(ALOG(GAMA2)/B2))/(C1/B1-C2/B2)
      RKA=(ALOG(GAMA1)/B1)-C1*RKB/B1

```

```

      GOTC888
50  GE=R*AT(M)*(RKA*X1*X2+RKB*X1*X2*(X1-X2))
888  RETURN
      END
C    THIS SUBROUTINE IS FOR VAN-LAAR EQUATION
      SUBROUTINE VANLAR(IN,GAMA1,GAMA2,X1,X2,VLA,VLB,GF,R,AT,M)
      DIMENSION AT(100)
      IN=IN+1
      IF(IN.GT.1)GOTO60
      VLA=(ALOG(GAMA1))*(1.+(X2*ALOG(GAMA2))/(X1*ALOG(GAMA1)))**2
      VLB=(ALOG(GAMA2))*(1.+(X1*ALOG(GAMA1))/(X2*ALOG(GAMA2)))**2
      GOTC777
60  GE=R*AT(M)*(X1+VLB*X2/VLA)*(X1/(X1+X2*VLB/VLA))*((VLB*X2/VLA)/(X1+
      1X2*VLB/VLA))*VLA
777  RETURN
      END
C    THIS SUBROUTINE IS FOR SCATCHARD-HAMMER EQUATION
      SUBROUTINE SCAHAM(GAMA1,GAMA2,X1,X2,MA,SHA,SHB,GF,R,AT,M,VL1,VL2)
      DIMENSION AT(100)
      Z1=X1/(X1+X2*(VL2/VL1))
      Z2=X2*(VL2/VL1)/(X1+X2*(VL2/VL1))
      MA=MA+1
      IF(MA.GT.1)GOTO70
      SHB=(ALOG(GAMA1)/(Z2*Z2*(1.-2.*Z1))-ALOG(GAMA2)/(2.*Z1*Z1*Z2*VL2/V
      1VL1))/(2.*Z1*VL1/VL2/(1.-2.*Z1))-((1.-2.*Z2)/(2.*Z2*VL2/VL1))
      SHA=ALOG(GAMA2)/(2.*Z1*Z1*Z2*VL2/VL1)-SHB*((1.-2.*Z2)/(2.*Z2*VL2/V
      1VL1))
      GOTC105
70  GE=R*AT(M)*(X1*(Z2*Z2*(SHA+2.*Z1*(SHB*(VL1/VL2)-SHA)))+Z2*(Z1*Z1*
      1SHB+2.*Z2*(SHA*(VL2/VL1)-SHB)))
105  RETURN
      END
CENTRY

```

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*****
*
*PROGRAM IT*
*
*****

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PROGRAM FOR OBTAINING APPROXIMATE RANGE OF AZEOTROPIC COMPOSITION BY
MATCHING ACTIVITY COEFFICIENTS AND PRODUCT OF ACTIVITY COEFFICIENTS AND
VAPOR PRESSURES

C LIQUID MOLAR VOLUMES ARE ASSUMED TO BE INDEPENDENT OF TEMP. AND PRE.
C FOR CALCULATION OF VIRIAL COEFFICIENTS KREGLESKI'S METHOD IS USED
C FOR VAPOR PRESSURE CALCULATION ANTOINE EQUATION IS USED
C UNITS OF R (MM OF HG)(C.C.)/(CM-MOLE)(K)

```

      DIMENSION U(10),VSTAR(5),ESTAP(5),TC(5),VC(10,10),AT(100)
1  FORMAT(1H1,/,50X,*SYSTEM- ETHYL ALCOHOL AND ETHYL ACETATE*,/,50X,2
19(1H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*T0=*,F6.1,2X,*X1=*,F7
2.4,2X,*X2=*,F7.4,/)
2  FORMAT(1H1,/,50X,*SYSTEM- BENZENE AND CYCLOHEXANE*,/,50X,21(1H*),/
1/,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*T0=*,F6.1,2X,*X1=*,F7.4,2X,*X
22=*,F7.4,/)
3  FORMAT(1H1,/,50X,*SYSTEM- HEXANE AND BENZENE*,/,50X,26(1H*),//,5X,
1,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*T0=*,F6.1,2X,*X1=*,F7.4,2X,*X2=*,F
27.4,/)
4  FORMAT(1H1,/,50X,*SYSTEM- METHANOL AND BENZENE*,/,50X,29(1H*),//,5
1X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*T0=*,F6.1,2X,*X1=*,F7.4,2X,*X2=*,
2,F7.4,/)
5  FORMAT(1H1,/,50X,*SYSTEM- METHYLCYCLOPENTANE AND BENZENE*,/,50X,30
1(1H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*T0=*,F6.1,2X,*X1=*,F7.
24,2X,*X2=*,F7.4,/)
6  FORMAT(1H1,/,50X,*SYSTEM- ETHANOL AND METHYLCYCLOHEXANE*,/,50X,27(
11H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*T0=*,F6.1,2X,*X1=*,F7.4
2,2X,*X2=*,F7.4,/)
7  FORMAT(F3.1,F4.2,F4.2,F4.2,F5.3)
8  FORMAT(F6.4,F6.4)
9  FORMAT(F8.4,F8.4)
11 FORMAT(F5.3,F7.1,F6.2)
12 FORMAT(F7.5,F8.3,F7.3,F7.5,F8.3,F7.3)
13 FORMAT(F4.1,F6.1)
14 FORMAT(5X,F5.1,3X,F7.1,5X,F7.4,5X,F7.4)

```

```

15  FORMAT(5X,F9.4,5X,F9.4)
16  FORMAT(2X,F7.4,6F12.4)
17  FORMAT(6F15.4)
19  FORMAT(F6.4,F6.4)
    R=80.06*760.
    READ7,F,RHO,RHOC,S,VOSTAR
    DO6 COMP=1,6
    N=1
    IN=0
    MN=0
    MA=0
    READ8,X1,X2
    READ9,VL1,VL2
    READ12,A1,B1,C1,A2,B2,C2
    DO333 II=1,2
    READ11,VSTAR(II),ESTAR(II),TC(II)
333  CONTINUE
    IF(MP.EQ.1)MQ=6
    IF(MP.EQ.2)MQ=4
    IF(MP.EQ.3)MQ=2
    IF(MP.EQ.4)MQ=2
    IF(MP.EQ.5)MQ=3
    IF(MP.EQ.6)MQ=2
    DO200 M=1,MQ
    READ13,T,P
    IF(MP.EQ.1)PRINT1,P,T,X1,X2
    IF(MP.EQ.2)PRINT2,P,T,X1,X2
    IF(MP.EQ.3)PRINT3,P,T,X1,X2
    IF(MP.EQ.4)PRINT4,P,T,X1,X2
    IF(MP.EQ.5)PRINT5,P,T,X1,X2
    IF(MP.EQ.6)PRINT6,P,T,X1,X2
    U(M)=T+273.16
    T1=B1*(1./(A1-ALOG(P)/2.303))-C1+273.16
    T2=B2*(1./(A2-ALOG(P)/2.303))-C2+273.16
    DO400 I=1,2
    CALL VIRIAL(U,RHO,S,VOSTAR,VSTAR,ESTAR,VC,TC,M,I)
400  CONTINUE
    CALL VPC(T,A1,B1,C1,A2,B2,C2,VP1,VP2)
    GAMA1=EXP(ALOG(P/VP1)+(F/(R*U(M)))*((VC(1,1)-VL1)*(P-VP1)))
    GAMA2=EXP(ALOG(P/VP2)+(F/(R*U(M)))*((VC(2,2)-VL2)*(P-VP2)))
    PRINT14,T,P,GAMA1,GAMA2
    IF(N-1)10,10,100
10   CALL RK(GAMA1,GAMA2,X1,X2,MN,RKA,RKB,GE,R,AT,M)
    PRINT15,RKA,RKB
    CALL VANLAR(IN,GAMA1,GAMA2,X1,Y2,VLA,VLB,GE,R,AT,M)
    PRINT15,VLA,VLB
    CALL SCAHAM(GAMA1,GAMA2,X1,X2,MA,SHA,SHB,GE,R,AT,M,VL1,VL2)
    PRINT15,SHA,SHB
    N=N+1
    GOTO200

```

```

100  RKA=RKA*U(M-1)/U(M)
      RKB=RKB*U(M-1)/U(M)
      VLA=VLA*U(M-1)/U(M)
      VLB=VLB*U(M-1)/U(M)
      SHA=SHA*U(M-1)/U(M)
      SHB=SHB*U(M-1)/U(M)
      READ 19,X1,PQ
222  X2=1.-X1
      RGMA1=EXP(X1*X2*(RKA+RKB*(X1-X2))+X2*(RKA*(X2-X1)+RKB*(4.*X1*X2-1.
1)))
      RGMA2=EXP(X1*X2*(RKA+RKB*(X1-X2))-X1*(RKA*(X2-X1)+RKB*(4.*X1*X2-1.
1)))
C    RGMA1,RGMA2-ACTIVITY COEFFICIENTS GIVEN BY REDLICH-KISTER EQUATION
C    FOR COMPONENT ONE AND TWO RESPECTIVELY
      VGMA1=EXP(VLA*X2*X2/(VLA*X1/VL1+X2)**2)
      VGMA2=EXP(VLB*X1*X1/(X1+VLB*X2/VLA)**2)
C    VGMA1,VGMA2-ACTIVITY COEFFICIENTS GIVEN BY VAN-LAAR EQUATION FOR
C    COMPONENT ONE AND TWO
      Z1=X1/(X1+X2*VL2/VL1)
      Z2=(X2*VL2/VL1)/(X1+X2*VL2/VL1)
      SGMA1=EXP(Z2*Z2*(SHA+2.*Z1*(SHB*VL1/VL2-SHA)))
      SGMA2=EXP(Z1*Z1*(SHB+2.*Z2*(SHA*VL2/VL1-SHB)))
C    SGMA1,SGMA2-ACTIVITY COEFFICIENTS GIVEN BY SCATCHARD-HAMMER EQUATION
C    FOR COMPONENT ONE AND TWO
      VRG1=VP1*RGMA1
      VRG2=VP2*RGMA2
      VVG1=VP1*VGMA1
      VVG2=VP2*VGMA2
      VSG1=VP1*SGMA1
      VSG2=VP2*SGMA2
      PRINT 16,X1,RGMA1,RGMA2,VGMA1,VGMA2,SGMA1,SGMA2
      PRINT 17,VRG1,VRG2,VVG1,VVG2,VSG1,VSG2
      IF(X1.GE.PQ)GOTO200
      X1=X1+0.0005
      GOTO222
200  CONTINUE
600  CONTINUE
      STOP
      END

```

C THIS SUBROUTINE CALCULATES THE VAPOUR PRESSURES OF THE COMPONENTS
 SUBROUTINE VPC(T,A1,B1,C1,A2,B2,C2,VP1,VP2)
 VP1=EXP(2.303*(A1-B1/(T+C1)))
 VP2=EXP(2.303*(A2-B2/(T+C2)))
 RETURN
 END

C THIS SUBROUTINE CALCULATES THE VIRIAL COEFFICIENTS
 SUBROUTINE VIRIAL(U,RHO,S,VOSTAR,VSTAR,ESTAR,VC,TC,M,I)
 DIMENSION U(10),VC(10,10),VSTAR(5),ESTAR(5),TC(5)

```

J=2
B=0.77+0.1325*(TC(I))**(0.334)
R1=(1.+S/(VSTAR(I)))*3
R2=(1.+VOSTAR/(VSTAR(I)))*3
R=1.987
C UNITS OF R - G.CAL,C.C./GM.-MOLE,OK
RPI=(RHO*ESTAR(I)*0.239)/(R*U(M))
RP2=S*RP1
WSTAR=VSTAR(I)*3
VC(I,I)=B*WSTAR*(1.-(R1-1.)*(EXP(RP1)-1.)-(R2-R1)*(EXP(RP2)-1.))
IF(I.LT.2)GOTO999
VC(I-1,J)=(2.*VC(I-1,I-1)*VC(I,I))/(VC(I,I)+VC(I-1,I-1))
999 RETURN
END

```

C THIS SUBROUTINE IS FOR REDLICH-KISTEP EQUATION
 SUBROUTINE RK(GAMA1,GAMA2,X1,X2,MN,RKA,RKB,GE,R,AT,M)

```

DIMENSION AT(100)
MN=MN+1
IF(MN.GT.1)GOTO50
B1=X2*X2
C1=(X1*X1*X2+5.*X1*X2*X2-X2)
B2=X1*X1
C2=(X1-X1*X2*X2-5.*X1*X1*X2)
RKB=((ALOG(GAMA1)/B1)-(ALOG(GAMA2)/B2))/(C1/B1-C2/B2)
RKA=(ALOG(GAMA1)/B1)-C1*RKB/B1
GOTC888
50 GE=R*AT(M)*(RKA*X1*X2+RKB*X1*X2*(X1-X2))
888 RETURN
END

```

C THIS SUBROUTINE IS FOR VAN-LAAR EQUATION
 SUBROUTINE VANLAR(IN,GAMA1,GAMA2,X1,X2,VLA,VLB,GE,R,AT,M)

```

DIMENSION AT(100)
IN=IN+1
IF(IN.GT.1)GOTO60
VLA=(ALOG(GAMA1))*(1.+(X2*ALOG(GAMA2))/(X1*ALOG(GAMA1)))*2
VLB=(ALOG(GAMA2))*(1.+(X1*ALOG(GAMA1))/(X2*ALOG(GAMA2)))*2
GOTC777
60 GE=R*AT(M)*(X1+VLB*X2/VLA)*(X1/(X1+X2*VLB/VLA))*((VLB*X2/VLA)/(X1+
1X2*VLB/VLA))*VLA
777 RETURN
END

```

C THIS SUBROUTINE IS FOR SCATCHARD-HAMMER EQUATION
 SUBROUTINE SCAHAM(GAMA1,GAMA2,V1,X2,MA,SHA,SHB,GE,R,AT,M,VL1,VL2)

```

DIMENSION AT(100)
Z1=X1/(X1+X2*(VL2/VL1))
Z2=X2*(VL2/VL1)/(X1+X2*(VL2/VL1))

```

```

MA=MA+1
IF(MA.GT.1)GOTO70
SHB=(ALOG(GAMA1)/(72*Z2*(1.-2.*Z1))-ALOG(GAMA2)/(2.*Z1*71*Z2*VL2/V
1L1))/(2.*Z1*VL1/VL2/(1.-2.*Z1))-(1.-2.*Z2)/(2.*Z2*VL2/V1L1))
SHA=ALOG(GAMA2)/(2.*Z1*Z1*Z2*VL2/VL1)-SHB*((1.-2.*Z2)/(2.*Z2*VL2/V
1L1))
GOTO105
70  GE=R*AT(M)*(X1*(Z2*Z2*(SHA+2.*71*(SHB*(VL1/VL2)-SHA)))+Y2*(Z1*Z1*(
1SHB+2.*Z2*(SHA*(VL2/VL1)-SHB))))
105  RETURN
      END
CENTRY

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*PROGRAM I'I*
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PREDICTION OF AZEOTROPIC BOILING TEMPERATURES AND COMPOSITION USING
REDLICH-KISTER, VAN-LAAR AND SCATCHARD-HAMMER EQUATIONS

C FOR CALCULATION OF VIRIAL COEFFICIENTS KREGLESKI'S METHOD IS USED
C LIQUID MOLAR VOLUMES ARE ASSUMED TO BE INDEPENDENT OF TEMP. AND PRE.
C FOR VAPOR PRESSURE CALCULATION ANTOINE EQUATION IS USED
C UNITS OF R (MM OF HG)(C.C.)/(CM-MOLE)(K)

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      DIMENSION U(10),VC(10,10),VSTAP(5),ESTAR(5),TC(5),AT(100),UU(20)
      R=80.06*760.
2002  FORMAT(100X,F10.7)
      1  FORMAT(/,15X,*R-K CONSTANTS*,//,6X,*GAMA1*,7X,*GAMA2*,9X,*PKA*,10X
1,*,*RKB*,10X,*T1*,11X,*T2*,/)
      2  FORMAT(/,15X,*VAN-LAAR CONSTANTS*,//,6X,*GAMA1*,7X,*GAMA2*,9X,*VLA
1*,10X,*VLB*,10X,*T1*,11X,*T2*,/)
5000  FORMAT(5X,3F10.4,5X,3F13.8)
      103  FORMAT(/,15X,*SCATCHARD-HAMMER CONSTANTS*,//,6X,*GAMA1*,7X,*GAMA2*
1,9X,*SHA*,10X,*SHB*,10X,*T1*,11X,*T2*,/)
      3  FORMAT(1H1,/,10X,*COMPARISON OF OBSERVED AND PREDICTED TEMPERATI
1RES BY R-K,VAN-LAAR AND SCATCHARD HAMMER EQUATIONS*,//)
      5  FORMAT(/,15X,*FOR ETHANOL*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*DELTA*,8X,*
1VC(1,2)*,/)
      8  FORMAT(/,15X,*FOR BENZENE*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*DELTA*,8X,*
1VC(1,2)*,/)
      320  FORMAT(/,15X,*FOR HEXANE*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*DELTA*,8X,*
1VC(1,2)*,/)
1002  FORMAT(F6.1)
1003  FORMAT(100X,F7.4)
      321  FORMAT(/,15X,*FOR METHANOL*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*DELTA*,8X,
1*VC(1,2)*,/)
      322  FORMAT(/,15X,*FOR METHYLCYCLOPENTANE*,/,8X,*VP1*,9X,*VC(1,1)*,7X,*
1DELTA*,8X,*VC(1,2)*,/)
2003  FORMAT(2X,F8.4,2X,F8.4,2X,F13.2,2X,F9.2,2X,F8.2,2X,F9.2,/)
2004  FORMAT(/,2F14.4,3F16.4,F15.4)
1005  FORMAT(F5.3,F5.3)
      6  FORMAT(/,15X,*FOR ETHYL ACETATE*,/,8X,*VP2*,9X,*VC(2,2)*,7X,*DELTA
1*,8X,*VC(1,2)*,/)

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11  FORMAT(/,15X,*FOR CYCLOHEXANE*,/,8Y,*VP2*,9X,*VC(2,2)*,7X,*DELTA*,
18X,*VC(1,2)*,/)
323  FORMAT(/,15X,*FOR METHYLCYCLOHEXANE*,/,8X,*VP2*,9X,*VC(2,2)*,7X,*
1DELTA*,8X,*VC(1,2)*,/)
1000  FORMAT(/,15X,*FOR BENZENE*,/,8Y,*VP2*,9X,*VC(2,2)*,7X,*DELTA*,8Y,*
1VC(1,2)*,/)
7  FORMAT(10X,F6.1,10X,F6.1,10X,F6.1,10X,F6.1,3X,F7.4,3X,F7.4,3X,F7.4
1,3X,F7.4,3X,F7.4,3Y,F7.4,/)
22  FORMAT(1H1,/,50X,*SYSTEM- ETHYL ALCOHOL AND ETHYL ACETATE*,/,50Y,2
19(1H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7
2.4,2X,*X2=*,F7.4,/)
33  FORMAT(1H1,/,50X,*SYSTEM- BENZENE AND CYCLOHEXANE*,/,50Y,21(1H*),/
1/,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2Y,*TO=*,F6.1,2X,*X1=*,F7.4,2X,*Y
22=*,F7.4,/)
314  FORMAT(1H1,/,50X,*SYSTEM- HEXANE AND BENZENE*,/,50X,26(1H*),//,5X,
1*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4,2Y,*X2=*,F
27.4,/)
316  FORMAT(1H1,/,50X,*SYSTEM- METHANOL AND BENZENE*,/,50X,22(1H*),//,5
1X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4,2X,*X2=*,
2,F7.4,/)
318  FORMAT(1H1,/,50X,*SYSTEM- METHYLCYCLOPENTANE AND BENZENE*,/,50X,30
1(1H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2Y,*X1=*,F7.
24,2X,*X2=*,F7.4,/)
319  FORMAT(1H1,/,50X,*SYSTEM- ETHANOL AND METHYLCYCLOHEXANE*,/,50X,27(
11H*),//,5X,*KNOWN POINT-*,2X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4
2,2X,*X2=*,F7.4,/)
77  FORMAT(/,5X,F7.4,5Y,F7.4,5X,F9.4,5Y,F8.4,5X,F8.2,5X,F8.2,/)
99  FORMAT(F4.1,F5.3,F5.3,F6.1)
222  FORMAT(F3.1,F4.2,F4.2,F4.2,F5.2,F6.2,F6.2,F6.2)
109  FORMAT(F7.5,F8.3,F7.3,F7.5,F8.2,F7.3)
666  FORMAT(F5.3,F7.1,F6.2)
66  FORMAT(/,5X,F8.2,5X,F9.2,5X,F8.2,5X,F9.2,5X,F9.4,/)
4  FORMAT(/,5X,*CHECK POINT*,5X,*P=*,F7.1,2X,*TO=*,F6.1,2X,*X1=*,F7.4
1,2X,*X2=*,F7.4,/)
104  FORMAT(/,2X,*APPROXIMATE TEMPERATURE EVALUATED=*,F8.2,/)
2000  FORMAT(10X,F5.1,10X,F7.4,10X,F7.4)
88  FORMAT(/,9X,*OBS TEMP*,10X,*RKTE*,12X,*VLTE*,12X,*SHTE*,/)
AQ=C.0000001
VL1=46.07/0.789
VL2=88.01/0.901
DO600MP=1,6
N=1
MN=0
IN=0
MA=C
MM=1
READ222,F,RHO,RHOC,S,VOSTAR,RKT,VLT,SH
READ109,A1,B1,C1,A2,B2,C2
DO333 II=1,2
READ666,VSTAR(II),ESTAR(II),TC(II)

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333  CONTINUE
      IF(MP.EQ.1)MQ=6
      IF(MP.EQ.2)MQ=4
      IF(MP.EQ.3)MQ=2
      IF(MP.EQ.4)MQ=3
      IF(MP.EQ.5)MQ=2
      IF(MP.EQ.6)MQ=2
      DO2 COM=1,MQ
      DIFMIN=100.
      JJ=0
      NN=0
      READ99,TO,X1,X2,P
      UU(M)=TO+273.16
      T1=B1*(1./((A1-ALOG(P)/2.303))-C1+273.16
      T2=B2*(1./((A2-ALOG(P)/2.303))-C2+273.16
      U(M)=TO+273.16
      IF(N-1)10,10,100
10    DO400 I=1,2
      CALL VIRIAL(U,RHO,S,VOSTAR,VSTAR,ESTAR,VC,TC,M,I)
400  CONTINUE
      DELTA=2.*VC(1,2)-VC(1,1)-VC(2,2)
      T=TC
      CALL VPC(T,A1,B1,C1,A2,B2,C2,VP1,VP2)
      IF(MP.EQ.1)PRINT22,P,TO,X1,X2
      IF(MP.EQ.1)GOTO44
101  VL1=78./0.879
      VL2=84./0.779
      IF(MP.EQ.2)PRINT33,P,TO,X1,X2
      IF(MP.EQ.2)GOTO44
      VL1=32./0.7924
      VL2=78./0.879
      IF(MP.EQ.3)PRINT316,P,TO,X1,X2
      IF(MP.EQ.3)GOTO44
      VL1=84./0.750
      VL2=78./0.879
      IF(MP.EQ.4)PRINT318,P,TO,X1,X2
      IF(MP.EQ.4)GOTO44
      VL1=46.07/0.789
      VL2=98./0.769
      IF(MP.EQ.5)PRINT319,P,TO,X1,X2
      IF(MP.EQ.5)GOTO44
      VL1=86./0.65937
      VL2=78./0.879
      IF(MP.EQ.6)PRINT314,P,TO,X1,X2
44  AA=ALOG(P/VP1)
      BB=F/(R*U(M))
      CC=(VC(1,1)-VL1)*(P-VP1)
      DD=P*DELTA*X2*X2
      IF(MP.EQ.1)PRINT5
      IF(MP.EQ.2)PRINT8

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IF(MP.EQ.3)PRINT321
IF(MP.EQ.4)PRINT322
IF(MP.EQ.5)PRINT5
IF(MP.EQ.6)PRINT320
PRINT66,VP1,VC(1,1),DELTA,VC(1,2),VL1
AAA=ALOG(P/VP1)
BBB=F/(R*U(M))
CCC=(VC(2,2)-VL2)*(P-VP2)
DDD=P*DELTA*X1*X1
IF(MP.EQ.1)PRINT6
IF(MP.EQ.2)PRINT11
IF(MP.EQ.6)PRINT1000
IF(MP.EQ.3)PRINT1000
IF(MP.EQ.4)PRINT1000
IF(MP.EQ.5)PRINT323
PRINT66,VP2,VC(2,2),DELTA,VC(1,2),VL2
GAMA1=EXP(ALOG(P/VP1)+(F/(R*U(M)))*((VC(1,1)-VL1)*(P-VP1)+P*DELTA
1*X2*X2))
GAMA2=EXP(ALOG(P/VP2)+(F/(R*U(M)))*((VC(2,2)-VL2)*(P-VP2)+P*DELTA
1*X1*X1))
CALL RK(GAMA1,GAMA2,X1,X2,MN,RKA,RKB,GE,R,AT,M)
PRINT1
PRINT77,GAMA1,GAMA2,RKA,RKB,T1,T2
CALL VANLAR(IN,GAMA1,GAMA2,X1,X2,VLA,VLB,GE,R,AT,M)
PRINT2
PRINT77,GAMA1,GAMA2,VLA,VLB,T1,T2
CALL SCAHAM (GAMA1,GAMA2,X1,X2,MA,SHA,SHB,GE,R,AT,M,VL1,VL2)
PRINT103
PRINT77,GAMA1,GAMA2,SHA,SHB,T1,T2
N=N+1
PRINT3
GOTO 200
100 READ1002,AT(M)
PRINT4,P,TO,X1,X2
PRINT104,AT(M)
PRINT88
AT(M-1)=RKT
555 RKA=RKA*AT(M-1)/AT(M)
RKB=RKB*AT(M-1)/AT(M)
AT(M-1)=AT(M)
RKT=AT(M)
ZZ1=RKA
ZZ2=RKB
CALL RK(GAMA1,GAMA2,X1,X2,MN,RKA,RKB,GE,R,AT,M)
444 U(M)=AT(M)
DO500 I=1,2
CALL VIRIAL(U,RHO,S,VOSTAR,VSTAR,ESTAR,VC,TC,M,I)
500 CONTINUE
DELTA=2.*VC(1,2)-VC(1,1)-VC(2,2)
T=AT(M)-273.16

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CALL VPC(T,A1,B1,C1,A2,B2,C2,VP1,VP2)
Y1=(VP1*GAMA1*X1)*EXP((VL1-VC(1,1))*(P-VP1)/(R*U(M)))/P
Y2=1.-Y1
C Y1,Y2-VAPOUR PHASE COMPOSITION OF COMPONENT ONE AND TWO
V1=((VL1-VC(1,1))*(P-VP1))/(R*AT(M))
V2=((VL2-VC(2,2))*(P-VP2))/(R*AT(M))
V=X1*V1+X2*V2
DELS1=R*AT(M)*ALOG(P/VP1)/(T1-AT(M))
DELS2=R*AT(M)*ALOG(P/VP2)/(T2-AT(M))
DELS0=X1*DELS1+X2*DELS2
W=X1*(ALOG(Y1/X1))+X2*(ALOG(Y2/X2))
AT1=T1*X1*DELS1/DELS0
AT2=T2*X2*DELS2/DELS0
AT3=GE/DELS0
AT4=R*AT(M)*V/DELS0
AT5=R*AT(M)*W/DELS0
AT(M)=AT1+AT2-AT3-AT4+AT5
BT=AT(M)-273.16
DIFF=ABS(BT-T0)
DIFXY=ABS(Y1-X1)
AW=ABS(W)
CHP=VP1*GAMA1*X1+VP2*GAMA2*X2
EE=AT(M)
FF=X1
GG=X2
OP=VC(1,1)
OQ=VC(2,2)
DR=VC(1,2)
OS=DELTA
HH=DIFXY
PP=AW
IF(DIFF.LT.DIFMIN)GOTO111
IF(DIFXY.LE.0.0001)GOTO1004
IF(AW.LE.AQ)GOTO1004
X1=X1+0.0005
X2=1.-X1
IF(X1.GE.1.0)GOTO1004
IF(JJ-1)555,55,102
1004 IF(NN-1)300,700,1001
111 DIFMIN=DIFF
IF(JJ-1)555,55,102
300 RKTE=EE
GMAR1=GAMA1
GMAR2=GAMA2
GER=GE
VPR1=VP1
VPR2=VP2
CHPR=CHP
REX1=FF
REX2=GG

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```

DT=CP
OU=CQ
OV=CR
OX=CS
DFX YR=HH
AWR=PP
READ1002,AT(M)
READ1005,X1,X2
AT(M-1)=VLT
DIFMIN=100.
JJ=JJ+1
MM=MM+1
NN=NN+1
55  VLA=VLA*AT(M-1)/AT(M)
    VLB=VLB*AT(M-1)/AT(M)
    AT(M-1)=AT(M)
    VLT=AT(M)
    ZZ1=VLA
    ZZ2=VLB
    CALL VANLAR(IN,GAMA1,GAMA2,X1,Y2,VLA,VLB,GE,R,AT,M)
    GOTC 444
700  VLTE=EE
    GMAV1=GAMA1
    GMAV2=GAMA2
    GEV=GE
    VPV1=VP1
    VPV2=VP2
    CHPV=CHP
    VEX1=FF
    VEX2=GG
    PT=CP
    PU=CQ
    PV=CR
    PX=CS
    DFX YV=HH
    AWV=PP
    READ1002,AT(M)
    READ1005,X1,X2
    AT(M-1)=SHT
    DIFMIN=100.
    JJ=JJ+1
    NN=NN+1
102  SHA=SHA*AT(M-1)/AT(M)
    SHB=SHB*AT(M-1)/AT(M)
    AT(M-1)=AT(M)
    SHT=AT(M)
    SHT E=EE
    GMA S1=GAMA1
    GMA S2=GAMA2
    GES=GE

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VPS1=VP1
VPS2=VP2
CHPS=CHP
SEX1=FF
SEX2=GG
QT=CP
QU=CQ
QV=CR
QX=CS
DFXYS=HH
AWS=PP
ZZ1=SHA
ZZ2=SHB
CALL SCAHAM (GAMA1,GAMA2,X1,X2,MA,SHA,SHB,GE,R,AT,M,VL1,VL2)
GOTC444
1001 PRINT7,UU(M),RKTE,VLTE,SHTE,REV1,REX2,VEX1,VEX2,SEX1,SEX2
C RKTE-AZEOTROPIC TEMPERATURE PREDICTED BY REDLICH-KISTER EQUATION
C VLTE-AZEOTROPIC TEMPERATURE PREDICTED BY VAN-LAAR EQUATION
C SHTE-AZEOTROPIC TEMPERATURE PREDICTED BY SCATCHARD-HAMMER EQUATION
C REX1,REX2-AZEOTROPIC COMPOSITION PREDICTED BY REDLICH-KISTER EQN.
C VEX1,VEX2-AZEOTROPIC COMPOSITION PREDICTED BY VAN-LAAR EQN.
C SEX1,SEX2-AZEOTROPIC COMPOSITION PREDICTED BY SCATCHARD-HAMMER EQN.
PRINT5000,DFXYR,DFXYV,DFXYS,AWP,AWV,AWS
C DFXYS-DIFFERENCE IN X AND Y OBTAINED USING REDLICH-KISTER EQN.
C DFXYV-DIFFERENCE IN X AND Y OBTAINED USING VAN-LAAR EQN.
C DFXYS-DIFFERENCE IN X AND Y OBTAINED USING SCATCHARD-HAMMER EQN.
PRINT2004,RKA,RKB,QT,QU,QV,QX
PRINT2003,GMAR1,GMAR2,GER,VPR1,VPR2,CHPR
PRINT2004,VLA,VLB,PT,PU,PV,PX
PRINT2003,GMAV1,GMAV2,GEV,VPV1,VPV2,CHPV
PRINT2004,SHA,SHB,QT,QU,QV,QX
PRINT2003,GMAS1,GMAS2,GES,VPS1,VPS2,CHPS
200 CONTINUE
600 CONTINUE
PRINT9
9 FORMAT(1H1)
STOP
END
C THIS SUBROUTINE CALCULATES THE VAPOUR PRESSURES OF THE COMPONENTS
SUBROUTINE VPC(T,A1,B1,C1,A2,B2,C2,VP1,VP2)
VP1=EXP(2.303*(A1-B1/(T+C1)))
VP2=EXP(2.303*(A2-B2/(T+C2)))
RETURN
END
C THIS SUBROUTINE CALCULATES THE VIRIAL COEFFICIENTS
SUBROUTINE VIRIAL(U,RHO,S,VOSTAR,VSTAR,ESTAR,VC,TC,M,I)
DIMENSION U(10),VC(10,10),VSTAR(5),ESTAR(5),TC(5)
J=2
B=0.77+0.1325*(TC(I))**(0.334)
R1=(1.+S/(VSTAR(I)))*3

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R2=(1.+VOSTAR/(VSTAR(I)))*3
R=1.987
C  UNITS OF R - G.CAL,C.C./GM.-MOLE,OK
RP1=(RHO*ESTAR(I)*0.239)/(R*U("))
RP2=S*RP1
WSTAR=VSTAR(I)**3
VC(I,I)=R*WSTAR*(1.-(R1-1.)*(EXP(RP1)-1.)-(R2-R1)*(EXP(RP2)-1.))
IF(I.LT.2)GOTO999
VC(I-1,I)=(2.*VC(I-1,I-1)*VC(I,I))/(VC(I,I)+VC(I-1,I-1))
999  RETURN
    END
C  THIS SUBROUTINE IS FOR REDLICH-KISTER EQUATION
    SUBROUTINE RK(GAMA1,GAMA2,X1,X2,MN,RKA,RKB,GE,R,AT,M)
    DIMENSION AT(100)
    MN=MN+1
    IF(MN.GT.1)GOTO50
    B1=X2*X2
    C1=(X1*X1*X2+5.*X1*X2*X2-X2)
    B2=X1*X1
    C2=(X1-X1*X2*X2-5.*X1*X1*X2)
    RKB=((ALOG(GAMA1)/B1)-(ALOG(GAMA2)/B2))/(C1/B1-C2/B2)
    RKA=(ALOG(GAMA1)/B1)-C1*RKB/B1
    GOTO888
50  GE=R*AT(M)*(RKA*X1*X2+RKB*X1*X2*(X1-X2))
    GAMA1=EXP(X1*X2*(RKA+RKB*(X1-X2))+X2*(RKA*(X2-X1)+RKB*(6.*X1*X2-1.
1)))
    GAMA2=EXP(X1*X2*(RKA+RKB*(X1-X2))-X1*(RKA*(X2-X1)+RKB*(6.*X1*X2-1.
1)))
888  RETURN
    END
C  THIS SUBROUTINE IS FOR VAN-LAAR EQUATION
    SUBROUTINE VANLAR(IN,GAMA1,GAMA2,X1,X2,VLA,VLB,GF,R,AT,M)
    DIMENSION AT(100)
    IN=IN+1
    IF(IN.GT.1)GOTO60
    VLA=(ALOG(GAMA1))*(1.+(X2*ALOG(GAMA2))/(X1*ALOG(GAMA1)))*2
    VLB=(ALOG(GAMA2))*(1.+(X1*ALOG(GAMA1))/(X2*ALOG(GAMA2)))*2
    GOTO777
60  GE=R*AT(M)*(X1+VLB*X2/VLA)*(X1/(X1+X2*VLB/VLA))*((VLB*X2/VLA)/(X1+
1X2*VLB/VLA))*VLA
    GAMA1=EXP(VLA*X2*X2/(VLA*X1/VLB+X2)*2)
    GAMA2=EXP(VLB*X1*X1/(X1+VLB*X2/VLA)*2)
777  RETURN
    END
C  THIS SUBROUTINE IS FOR SCATCHARD-HAMMER EQUATION
    SUBROUTINE SCAHAM(GAMA1,GAMA2,V1,X2,MA,SHA,SHB,GE,R,AT,M,VL1,VL2)
    DIMENSION AT(100)
    Z1=X1/(X1+X2*(VL2/VL1))
    Z2=X2*(VL2/VL1)/(X1+X2*(VL2/VL1))
    MA=MA+1
    IF(MA.GT.1)GOTO70

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      SHB=(ALOG(GAMA1)/(Z2*Z2*(1.-2.*Z1))-ALOG(GAMA2)/(2.*Z1*Z1*Z2*VL2/V
1L1)))/((2.*Z1*VL1/VL2/(1.-2.*Z1))-((1.-2.*Z2)/(2.*Z2*VL2/V
      SHA=ALOG(GAMA2)/(2.*Z1*Z1*Z2*VL2/VL1)-SHB*((1.-2.*Z2)/(2.*Z2*VL2/V
1L1))
      GOTC105
70  GE=R*AT(M)*(X1*(Z2*Z2*(SHA+2.*Z1*(SHB*(VL1/VL2)-SHA)))+Y2*(Z1*Z1*
1SHB+2.*Z2*(SHA*(VL2/VL1)-SHB)))
      GAMA1=EXP(Z2*Z2*(SHA+2.*Z1*(SHB*VL1/VL2-SHA)))
      GAMA2=EXP(Z1*Z1*(SHB+2.*Z2*(SHA*VL2/VL1-SHB)))
105  RETURN
      END
CENTRY

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SHB=(ALOG(GAMA1)/(72*Z2*(1.-2.*Z1))-ALOG(GAMA1)/(2.*Z1*Z1*Z1*VL1/
1L1))/(2.*Z1*VL1/VL2/(1.-2.*Z1))-(1.-2.*Z2)/(2.*Z2*VL2/VL1))
SHA=ALOG(GAMA2)/(2.*Z1*Z1*Z2*VL2/VL1)-SHB*((1.-2.*Z2)/(2.*Z2*VL2/
1L1))
GOTC105
70 GF=R*AT(M)*(X*(Z2*Z2*(SHA+2.*Z1*(SHB*(VL1/VL2)-SHA)))+Y2*(Z1*Z1*
1SHB+2.*Z2*(SHB*(VL2/VL1)-SHB)))
GAMA1=EXP(Z2*Z2*(SHA+2.*Z1*(SHB*VL1/VL2-SHA)))
GAMA2=EXP(Z1*Z1*(SHB+2.*Z2*(SHB*VL2/VL1-SHB)))
105 RETURN
END
CFNTRY

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